# Synthesis and Coordination Chemistry of Triazacyclohexanes and Orthoamides

vorgelegt von
Diplom-Chemiker
Guido Seifert

Dem Fachbereich 5 - Chemie -
der Technischen Universität Berlin
zu Erlangung des akademischen Grades
Doktor der Naturwissenschaften
Dr. rer. nat.
genehmigte Dissertation

Promotionsausschuß:

| | |
|---|---|
| Vorsitzender: | Prof. Dr. rer. nat. G. Findenegg |
| Berichter: | Dr. habil. rer. nat. Randolf Köhn |
| Berichter: | Prof. Dr. rer. nat. H. Schumann |

Tag der mündlichen Prüfung: 22. Dezember 1999

Berlin 1999
D 83

**Abstract**

This thesis describes the extension of the coordination chemistry of triazacyclohexanes to new copper complexes and to new ligands with similar coordination geometry, i.e. the orthoamides 13-alkyl-1,5,9-triazatricyclo[7.3.1.$0^{5,13}$]-tridecanes (R-TATC) and unsymmetrically substituted triazacyclohexanes. By treatment of the literature known $[TATC]^+$ cation with Li, Na, or K alkylating reagents several new RTATC (R = Ph, Bz, $CH_2SiMe_3$, 4-$^t$Bu-Ph$CH_2$) have been prepared and characterized. With these and the previously known ligands HTATC and MeTATC complexes of Cr(III), Fe(III), Cu(II), and Zn(II) have been made and their properties have been compared with those of the analogous 1,3,5-trialkyl-1,3,5-triazacyclohexane ($R_3$TAC) complexes. It shows that the structural, chemical, and physical properties of the RTATC complexes are quite similar to those of the $R_3$TAC complexes.

[($R_3$TAC)Cu($PPh_3$)]$BF_4$ complexes with R = $^i$Pr, Bz, Cy, and (S)-PhMeCH have been prepared and characterized. The Cu(I) complexes are diamagnetic and therefore ideal for NMR spectroscopical analysis. The $\eta^3$-coordination of the ligand can be deduced from the discrimination of the endo- and exo-protons of the TAC-ring, which are in fast exchange in the free ligand. From the form of the ring signals a more symmetrical $\eta^3$-coordination for the $^i$Pr$_3$TAC complex and a slightly distorted $\eta^3$-coordination for the Bz$_3$TAC complex can be expected. This could be verified by x-ray crystal structures of both complexes.

A new Cu(II) complex was found when excess $Me_3$TAC was reacted with $CuCl_2$: ($Me_3$TAC)$_2$$CuCl_2$. The unusual coordination geometry leads to a slow reduction to Cu(I). A crystal structure of the reduction product revealed an unusual $[Cu_2Cl_4]^{2-}$. It shows the first Cu-Cu cuprophilic interaction in an anion which must be stronger than the electrostatic repulsion within the dianion.

Synthesis of triazacyclohexanes with a mixture of two amines in a suitable solvent such as ethanol or exploitation of equilibria between $R_3$TAC and R′$NH_2$ above 100 °C yields mixtures of unsymmetrically substituted $R_2$R′TAC which could be separated by various methods below 100°C. The pure and dry unsymmetrical $R_2$R′TAC are stable at room temperature and even at higher temperatures for short periods and can best be identified by their very characteristic $^{13}$C NMR signals for the ring carbon atoms. This way a couple of examples for basically three different types of unsymmetrically substituted $R_2$R′TAC could be prepared: simple $R_2$R′TAC with small hydrocarbon substituents ($Me_2$BzTAC, $Me_2$OctTAC), $R_2$(R′X)TAC with a substituent bearing a functional group ($Me_2$(EtOH)TAC, $Me_2$(EtCN)TAC), and two triazacyclohexanes linked by a short bridge $R_2$TAC-R'-$R_2$TAC ($Me_2$TAC-$CH_2$Ph$CH_2$-$Me_2$TAC), $^t$Bu$_2$TAC-$CH_2$Ph$CH_2$-$^t$Bu$_2$TAC).

**Abstract**

Diese Arbeit beschreibt die Erweiterung der Koordinationschemie der Triazacyclohexane durch neuartige Kupferkomplexe sowie anderer Ligandensysteme mit ähnlicher Koordinationsgeometrie, wie z.B. den Orthoamiden (13-Alkyl-1,5,9-triazatricyclo[7.3.1.$0^{5,13}$]-tridecanen, RTATC). Bei der Umsetzung des literaturbekannten $[TATC]^+$ Kations mit Li, Na oder K-Alkylverbindungen konnten ein Reihe neuartiger RTATC (R = Ph, Bz, $CH_2SiMe_3$, 4-$^t$Bu-Ph$CH_2$) gewonnen und charakterisiert werden. Mit diesen neuen und den in der Literatur bereits bekannten Liganden HTATC und MeTATC wurden Cr(III)-, Fe(III)-, Cu(II)- und Zn(II)-Komplexe hergestellt und deren Eigenschaften mit den analogen Komplexen der 1,3,5-trialkyl-1,3,5-triazacyclohexane ($R_3$TAC) verglichen. Es zeigte sich, daß sowohl die strukturellen als auch die physikalischen und chemischen Eigenschaften der RTATC Komplexe sehr ähnlich denen der $R_3$TAC Komplexes sind.

Es wurden $[(R_3TAC)Cu(PPh_3)]BF_4$ Komplexe mit R = $^i$Pr, Bz, Cy, und (S)-PhMeCH hergestellt und charakterisiert. Diese Komplexe sind diamagnetisch und daher sehr geeignet, mit NMR-spektroskopischen Methoden untersucht zu werden. Die $\eta^3$-Koordination der Liganden kann aus der Aufspaltung der endo- und exo-Protonen des TAC-Ringes geschlossen werden. Deren Signale fallen in den freien Liganden zusammen. Aus der Form der Signale kann auf eine etwas mehr symmetrische Koordination im Fall des $^i$Pr$_3$TAC Komplexes und auf eine leichte Verzerrung im Fall des Bz$_3$TAC Komplexes geschlossen werden. Das konnte durch eine Röntgenkristallstrukturanalyse bestätigt werden.

Ein neuartiger Cu(II)-Komplex wurde gefunden, als $CuCl_2$ mit einem Überschuß von $Me_3$TAC umgesetzt wurde: $(Me_3TAC)_2CuCl_2$. Aus dessen ungewöhnlicher Struktur resultiert, daß das Cu(II) in diesem Komplex langsam durch $Me_3$TAC zu Cu(I) reduziert wird. Eine Röntgenkristallstruktur des Reduktionsproduktes zeigte das sehr ungewöhnliche $[Cu_2Cl_4]^{2-}$ Anion. Es ist das erste Beispiel für eine Cu-Cu cuprophilischen Wechselwirkung in einem Anion, die daher stärker sein muß, als die elektrostatische Abstoßung.

Die Synthese von Trizacyclohexanen in einer Mischung aus zwei Aminen in einem passenden Lösungsmittel, wie z.B. Ethanol, oder die Ausnutzung des Gleichgewichts zwischen $R_3$TAC und R′$NH_2$ oberhalb von 100 °C, ergibt eine Mischung von unsymmetrisch substituierten Triazacyclohexane, die durch eine Reihe verschiedener Methoden unterhalb von 100 °C getrennt werden konnten. Die reinen und trockenen unsymmetrisch substituierten TAC sind bei Raumtemperatur, für kurze Zeit auch bei höheren Temperaturen, stabil und können am besten durch die charakteristischen $^{13}$C-NMR Signale ihrer Ring-Kohlenstoffatome identifiziert werden. Auf diese Weise konnten drei verschiedene Klassen von unsymmetrisch substituierten Triazacyclohexanen hergestellt und charakterisiert werden: Einfache $R_2$R′TAC mit kleinen aliphatischen oder aromatischen Substituenten ($Me_2$BzTAC, $Me_2$OctTAC), $R_2$(R′X)TAC mit einem funktionalisierten Substituenten ($Me_2$(EtOH)TAC, $Me_2$(EtCN)TAC) und zwei über eine kurze Brücke verbundene Triazacyclohexane $R_2$TAC-R'-$R_2$TAC ($Me_2$TAC-$CH_2$Ph$CH_2$-$Me_2$TAC), $^t$Bu$_2$TAC-$CH_2$Ph$CH_2$-$^t$Bu$_2$TAC).

**Acknowledgements**

This thesis has been done at the *Institut für Anorganische und Analytische Chemie und Lehrerbildung in der Chemie der Technischen Universität Berlin* and of course, during this work I met several people who helped me in one or another situation, I want to thank now. First of all there is:

## Dr. R. D. Köhn

He was not only a source for valuable informations. Working for such a long time with me is prove enough for his almost godly patience. Next there is:

## Prof. Dr. H. Schumann

He gave me more than one good advice and allowed generously the use of the resources of his working group.

Special thanks to:

## Dr. G. Kociok-Köhn

She invested much work in the not always perfect crystals I gave her. Her devotion to the x-ray crystallographical arts I owe the x-ray crystal structures in this work. Of course she could not have worked for me without the agreement of:

## Prof. Dr. A. Filippou

Thanks for the usage of his x-ray crystallographical resources and time.

Special thank, too, for

## Dr. Matthias Haufe

What can I say? Working with him was much fun (at least for me).

Of course, there are many more I have to thank: Dr. S. Mihan (BASF; Polymerization) M. Dettlaff, Dr. H.-J. Kroth, Dr. D. Zeigan (NMR); S. Imme (IR, Raman and Jokes); D. Bernhard, U. Kieper (CHN, AAS) and most of the other staff of the institute.

# Contents

# List of Figures

# List of Tables

# 1 Introduction and Overview

The formation of 1,3,5-triazacyclohexanes from primary amines and formaldehyde has been known for more than one hundred years. The first reliable descriptions for the preparation of 1,3,5-trimethyl-1,3,5-triazacyclohexane ($Me_3TAC$) were reported in the mid 1890's [1]. At

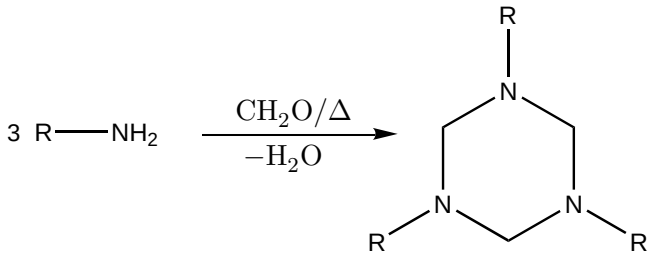



Figure 1: General route to symmetrical 1,3,5-trialkyl-1,3,5-triazacyclohexanes ($R_3TAC$).

the same time (1893-1895) the preparation and the chemistry of several other derivates of $R_3TAC$ where described [2]. However, the coordination chemistry of the 1,3,5-trialkyl-1,3,5-**t**ri**a**za**c**yclohexanes ($R_3TAC$) was surprisingly scarce, for such an old and easily available compound class. Figure 2. shows three examples of $\eta^3$-bonded $R_3TAC$ complexes [3, 4, 5]. There

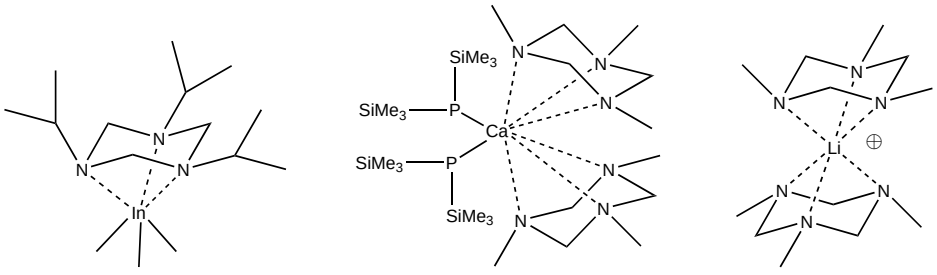
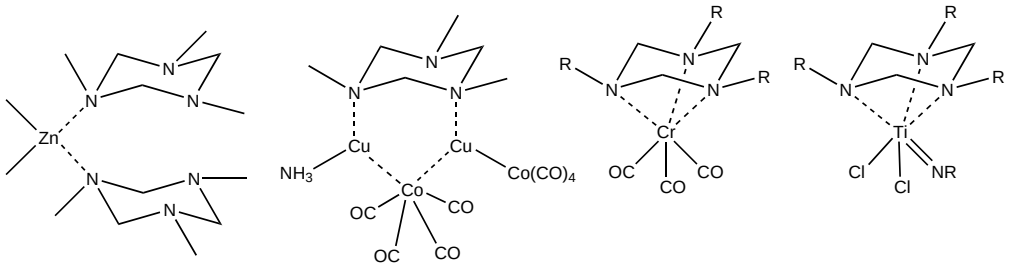



Figure 2: Three examples of main group element complexes of $R_3TAC$

were even less data available for transition metal complexes of $R_3TAC$. In publications from 1959 [6] and 1966 [7] the existence of $\eta^3$-complexes of chromium and molybdenum was postulated, based solely on IR-data. Better characterized were some $\eta^1$-complexes of zinc and cadmium with $R_3TAC$ [8] and a $\mu$-complex of copper and cobalt [9]. However, the interest in $R_3TAC$ as ligand seems to be growing rapidly lately as two new publications may indicate [10, 11] (see fig. 3 p. 12). This was the situation when our group




1990 1991 1998 1999

Figure 3: Examples of an $\eta^1$-, a $\mu^2$-, and a $\eta^3$-transition group element complex of $R_3TAC$ and the quite new titanium $R_3TAC$ complexes [10, 11]

began to take interest in this field in 1992. Our main goal was the development of a functional and structural model system for the Phillips catalyst. Therefore, chromium complexes of $R_3TAC$ where the primary objective of our research. The three nitrogen atoms of these ligands standing in close proximity were supposed to mimic the hard donor atom environment of an active chromium center on a silicate surface of a Phillips catalyst. By variation of the alkyl substituents on the nitrogen atoms "fine tuning" of important properties of the complexes such as solubility, steric load, and bond strength were intended. Though some very promising results were observed with the polymerizations of ethylene, propylene, and styrene using these complexes as catalyst, one aspect of our work, however, was somewhat

dissatisfying. The strong paramagnetism of chromium(III) hindered analysis of the complexes by NMR-spectroscopy. The very low solubility of the $R_3$TAC complexes in all common solvents inhibited the growth of suitable crystals for x-ray crystallography. Those unfortunate properties did not allow to get sufficient structural data for the complexes.

So additionally to the chromium complexes and their catalytic use, several other questions arose during this work. First of all, several non-chromium complexes were prepared for their crystallizing or NMR-spectroscopical properties to gain further insight into the structures of $\eta^3$-TAC complexes. Figure

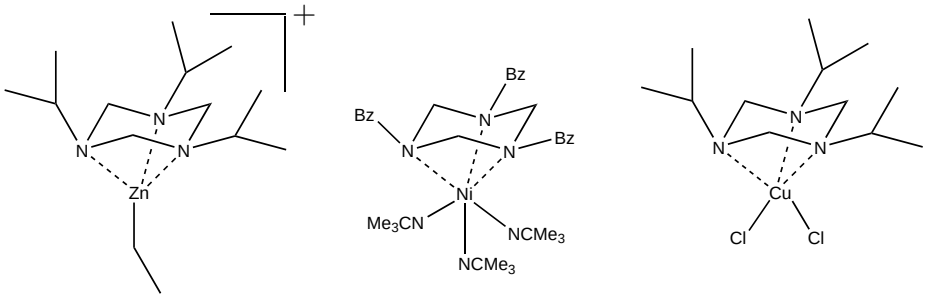


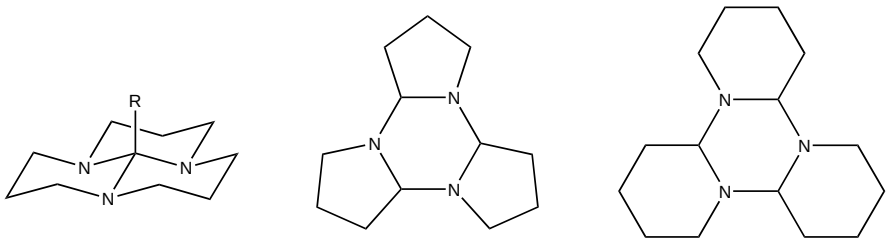

Figure 4: Some examples of in our group prepared and characterized transition group element complexes of $^{i}Pr_3$TAC and $Bz_3$TAC.

4 shows a small selection of the $R_3$TAC complexes made and characterized in our group [12, 13]. Especially the $Zn^{2+}$ complex, due to its diamagnetism, allowed a deeper understanding of $\eta^3$-bonded transition metal complexes of $R_3$TAC by NMR-spectroscopy [14].

Since all the considerations above about the task of $R_3$TAC in chromium complexes are mainly based on the geometrical arrangement of three nitrogen atoms therein, not only $R_3$TAC complexes were considered as possible candidates for modeling the characteristics of a Phillips catalyst. Figure 5

shows some other ligands with similar $N_3$-core structure like the $R_3$TAC.

Based on this, the first task in this work was to prepare and characterize some of these alternative ligands and their complexes for comparison with the in the mean time quite well elaborated chemistry of $R_3$TAC and its complexes. From the examples in figure 5, only with the first one (RTATC)




RTATC C5TAC C6TAC

Figure 5: Some examples of compounds with similar $N_3$-core structures as in the $R_3$TAC ligands.

comprehensive studies were made. Though the 1-pyrroline trimer (C5TAC) was readily available in a one step synthesis [15], its thermal and acid lability and the limited possibilities to vary the surrounding of the nitrogen atoms, make this sort of compounds considerably harder to handle and in terms of the desired ligand tuning less promising than the RTATC class. Therefore, after some unsuccessful attempts with C5TAC to make a Cu(I)-complex analogous to the ones in figure 35 (p. 43) working on this compound class was given up early.

The RTATC ligands were expected to give much better results. Prior to this work, only RTATC with R = H, R = Me and R = Et has been known in literature and only two $\eta^3$-molybdenum complexes were reported [16]. This was a good base to start the work and resulted quickly in the successful preparation of chromium(III)chloride complexes of HTATC and MeTATC.

Unfortunately these complexes were even less soluble than the comparable $Me_3TACCrCl_3$ complex. Larger substituents R were supposed to improve the solubility of the $RTATCCrCl_3$ complexes. But since the already known synthesis for HTATC and MeTATC were not applicable for larger R, a more general route to RTATC had to be developed.

Unfortunately the chromium complexes of the newly prepared RTATC-ligand (R = Bu, Ph, Bz, $CH_2Si(CH_3)_3$) were not notably more soluble than the HTATC or MeTATC complexes. The solubility of the TATC-chromium complexes was in all cases worse than the solubility of analogous triazacyclohexane complexes with comparable substituents. Most of the characterization of RTATC complexes had to be done on complexes of copper or zinc.

Since it became more and more obvious that from none of the other ligands as favorable properties can be expected as from the triazacyclohexanes, at least not in consideration as a possible model system for the Phillips catalyst or as economical usable polymerization catalyst, the interest in these compounds gradually vanished.

At the same time, for the copper complexes another very interesting aspect became apparent. Though the primary task of copper, namely Cu(I) and zinc in $R_3TAC$ and RTATC complexes was to provide structural information which were much harder to obtain from the chromium complexes, $R_3TAC$/Cu(I) complexes have a structural similarity to certain classes of oxygen activating bio-inorganic complex systems, too.

In these systems the reversible binding of CO and $O_2$ to binuclear copper(I) complexes is described, which mimics to a significant extent a number of properties of the copper-containing dioxygen protein hemocyanin. One of these complexes $[Cu_2(L)O_2]^{2+}$ where L is a dinucleating ligand containing hydrocarbon linkers which connect two tridentate donor bis[2-(2-

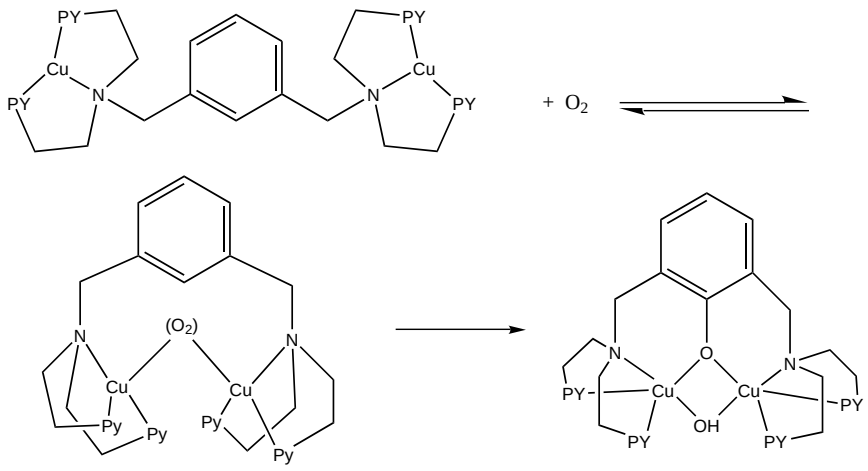



Figure 6: An oxygen activating Cu(I) complex Karlin [17] PY = 2-pyridyl

pyridyl)ethyl]amine units (figure 6, p. 16) is described by Karlin et. al. [17]. At $-78\,^{\circ}\mathrm{C}$ in dichlormethane this tricoordinated dicopper(I) complex $[Cu_2(L)]$ reacts reversibly with $O_2$ to give complexes formulated as $[Cu_2(N_6)(O_2)]^{2+}$. The chemistry of copper complexes of triazacyclohexanes or orthoamides became after the preparation and characterization of $R_3TAC$ analogues the second main topic in this thesis.

The third one has been inspired by a study by Tolman and coworkers. In this study a system $[Cu_2(L)O_2]^{2+}$ with similar properties like in the above mentioned complex by Karlin is described. However, in this case the ligand L is a hydrocarbon bridged tridentate triazacyclononane (figure 7) [18]. The m-xylylene bridged bis[2-(2-pyridyl)ethyl]amine units in the Karlin complex and the linked triazacyclononane units in the Tolman complex kindled the interest in a combination of both ligands: m-xylylene bridged triazacyclohexanes. Finally the attempts to prepare these ligands lead to the preparation of unsymmetrically substituted triazacyclohexanes in general. This, however, proved to be much more difficult than expected. Though a great number of

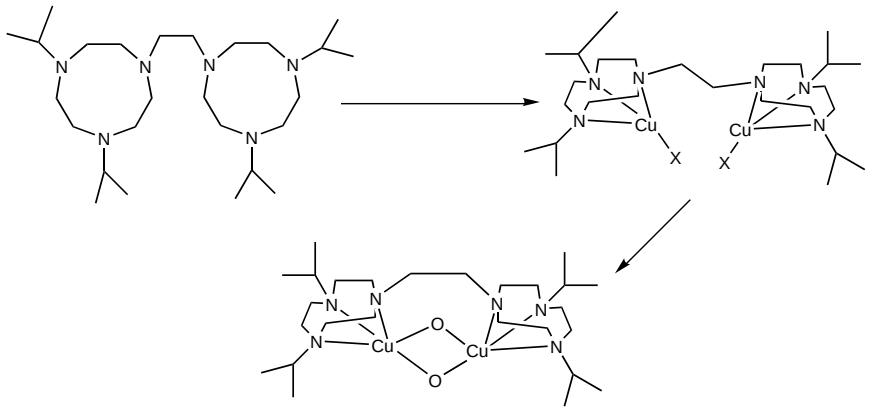



Figure 7: Oxygen activating Cu(I)-triazacyclononane complex by Tolman et. al. X = $CH_3CN$

different triazacyclohexanes have been known for almost 100 years, virtually nothing can be found in literature about the synthesis of unsymmetrically substituted R′$R_2$TAC or R′R″R‴TAC. The comparatively few exceptions where an unsymmetrically substituted triazacyclohexane is discussed in literature were about special cases of hetero substituted R′$R_2$TAC (figure 8) with synthetic routes working only for one specific compound. Generalization of these syntheses to obtain the desired alkyl substituted R′$R_2$TAC is not possible. During the work on the bridged triazacyclohexanes, apart from the possible bio-inorganic aspect, another application for a class of R′$R_2$TACs became apparent. Triazacyclohexanes with one OH- or $NR_2$-functionalized substituent as ligands for chromium(III)-compounds could work as building blocks of a new variant of Phillips catalyst like TAC-complexes. Under consideration of the possible prospect compared with the very small amount of information available about them, the third part of this work mainly concentrates on the preparation and characterization of several classes of unsymmetrical substituted R′$R_2$TAC.

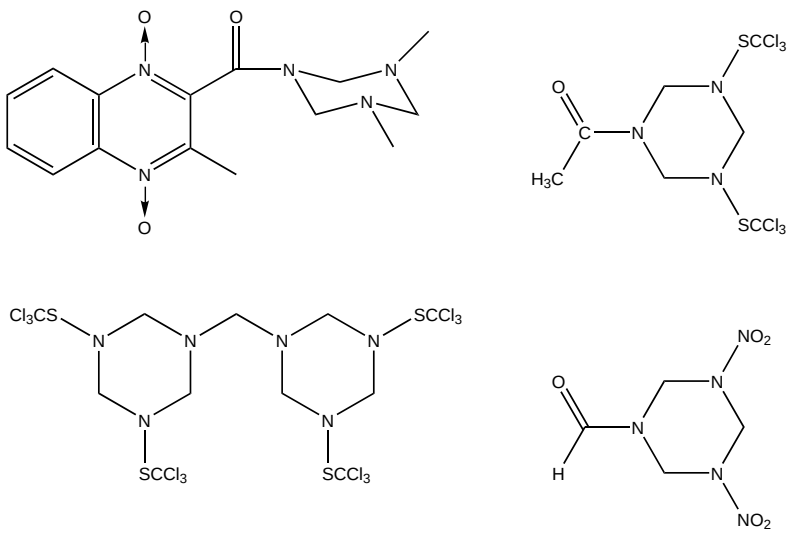



Figure 8: Examples of unsymmetrically hetero-substituted $R_2R'TAC$ in literature [2]

Finally, the topics worked upon in this thesis can be summarized as follows:

- Preparation and characterization of $R_3TAC$ analogues and complexes with some selected transition metals.
- Preparation and characterization of Cu(I) and Cu(II) complexes of $R_3TAC$.
- Preparation and characterization of unsymmetrically substituted triazacyclohexanes.

# 2 Discussion and Results

## 2.1 Synthesis of 13-Alkyl-1,5,9-triazatricyclo[7.3.1.0$^{5,13}$]-tridecanes RTATC

13-alkyl-1,5,9-triazatricyclo[7.3.1.0$^{5,13}$]-tridecanes (RTATC) with R = H or R = Me have been prepared for the first time by Weisman and Atkins [19, 20]. However, the route they used was not only tedious involving several steps, but also restricted to only small substituents like H, Me or Et. In a later work another, easier route to HTATC **1** and indirectly to MeTATC **2** and EtTATC was described [21] (see figure 9), but the restriction to only small substituents remained.

HTATC was prepared according to literature methods [21]. The preparation of MeTATC, though also possible according to the path outlined in figure 9, was done with the method newly developed in this thesis.

This method had to be developed, because chromium chloride complexes of HTATC and MeTATC proved to be extremely insoluble in all common solvents. So the idea was to improve their solubility by using RTATC ligands substituted with larger organic substituents R. The easiest way to get those ligands seemed to be the alkylation of 1,5,9-triazatricyclo[7.3.1.0$^{5,13}$]tridecan-13-ylium cation **3** (see figure 10). Indeed, the alkylation of TATCBr with TMSLi ($LiCH_2Si(CH_3)_3$) or n-BuLi in THF went smoothly with a yield of up to 65 %. However, the process of purifying the hygroscopic TATCBr was very difficult and for larger quantities hardly feasible. In deed, for 5 g of pure TATCBr more than 5 l of dry methylene chloride and 5 l of dry diethylether had to be used in a process of repeated dissolution and precipitation. Using a less pure TATCBr, though thoroughly dried in high vacuum for several days, gave a much lower yield with $LiCH_2Si(CH_3)_3$ and no product at all with PhLi

and BzLi. Replacing the $Br^-$ anion with $BF_4^-$ [21], gives $TATCBF_4$ which can be easily purified by recrystallization and is not hygroscopic. Unfortunately, all attempts to use $TATCBF_4$ instead of the bromide in the alkylation reactions revealed the TATC cation to be quite resistant to nucleophilic addition and $BF_4^-$ is attacked earlier than $TATC^+$ by the used lithium alkyls,

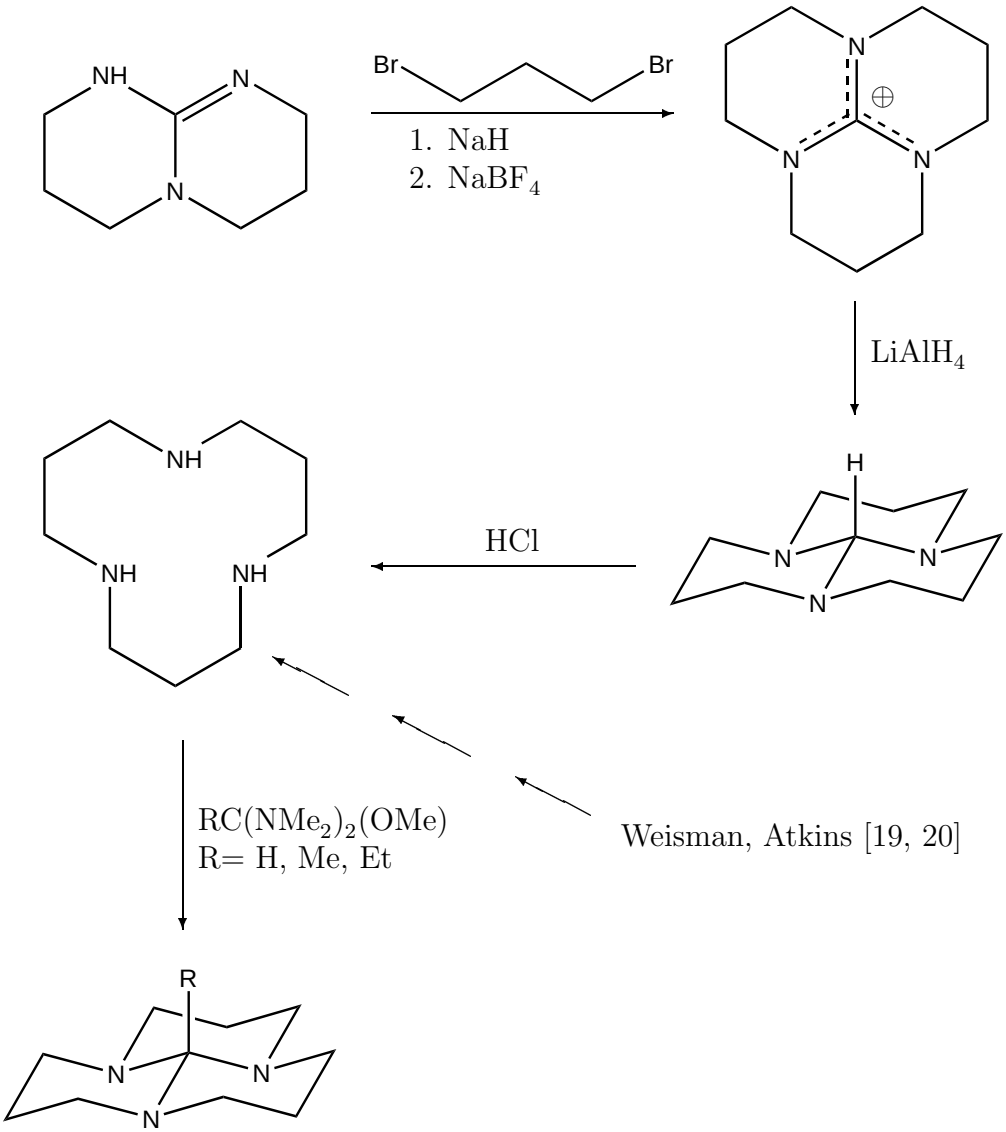



Figure 9: Literature known routes to RTATC (Alder, Weisman [21])

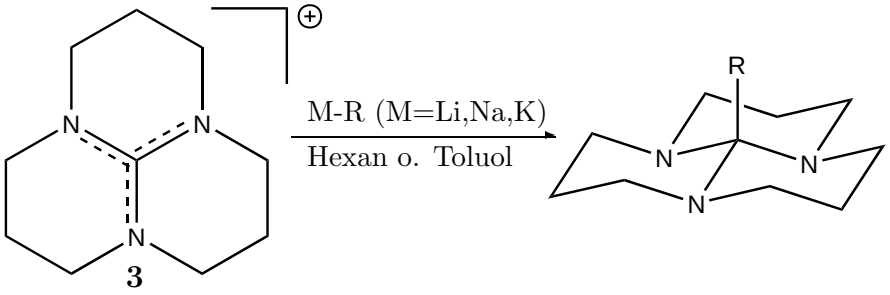



Figure 10: Alkylation of the guadinium cation $TATC^+$

Grignard- or copper alkylating reagents under the given conditions.

The replacement of the $BF_4^-$ anion with $BPh_4^-$ did prevent reactions with the anion, but the solubility of $\mathbf{3}^+BPh_4^-$ is extremely low in solvents tolerant towards alkylating reagents. No reaction at all could be observed in experiments using the $\mathbf{3}^+BPh_4^-$ as suspension with lithium alkyls in several solvents. The reaction worked only,when the lithium alkyls were replaced by potassium alkyls, but still with much lower yields than acceptable. A hint that now the solubility really was the limiting factor for the reaction is the fact, that a slightly better yield could be obtained by using alkyl sodium compounds. But not the increase in yield make sodium alkyls the better choice to use: in all reactions, regardless whether sodium or potassium alkyls have been used, up to 50% of $TATCBPh_4$ remained unchanged. So the considerable advantage of using sodium alkyls is the higher solubility of the $NaBPh_4$ compared to $KBPh_4$, which allows to remove the byproduct from the unchanged $TATCBPh_4$ and to recycle the valuable educt.

In the special case of PhTATC **4** and MeTATC **17** a second route was found. $Me_3SiCH_2TATC$ **5** can be cleaved with water to give MeTATC. Of course, normally this method is too expensive and much more time consuming than the direct methylation of TATCBr with MeLi. But by cleaving with $D_2O$ it is possible to introduce exactly one deuterium atom into the methyl

group of MeTATC (fig. 11) which may become important for $^2$H-NMR studies. For PhTATC, diphenyl-mercury with sodium and TATCBPh$_4$ in hexane

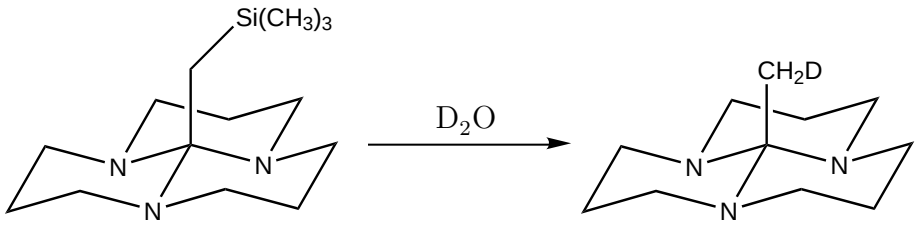



Figure 11: Cleavage of $(CH_3)_3SiCH_2TATC$ with $D_2O$

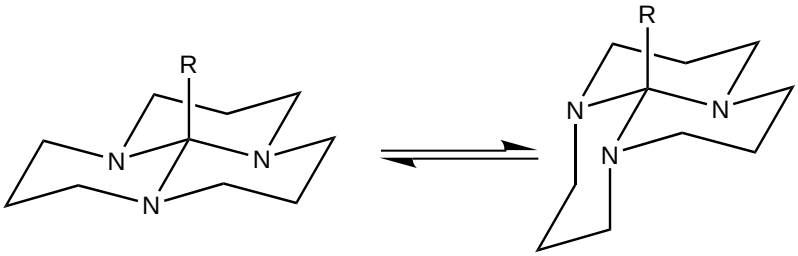
gave the highest yield in one experiment with almost 60% of PhTATC. However, the yield in the sodium alkyl as much as in the diphenyl-mercury reactions fluctuated very strongly depending on the solvent, temperature and/or reaction time from 0% up to 60% yield.

None of these methods are optimized yet and though the mercury-method once gave the highest yield, there still is much potential in varying the solvent, anion or alkali metal to improve the first route and to avoid the poisonous diphenyl-mercury and its waste products.

Nevertheless, no further attempts have been made to optimize the synthesis of RTATC, when from earlier experiments enough material was obtained to go on with the synthesis and characterization of several RTATC complexes.

### 2.1.1 Characterization of RTATC

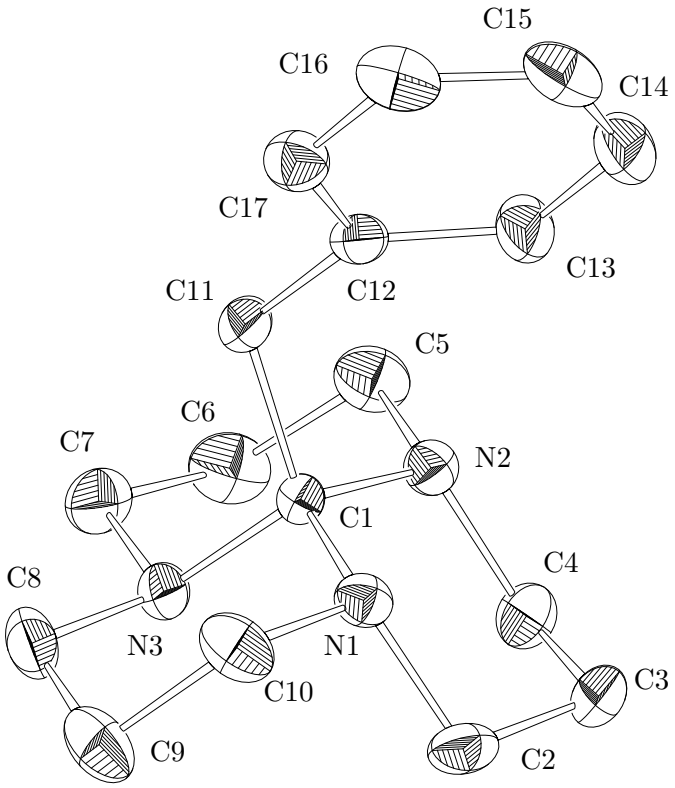
PhTATC **20** and BzTATC **6** are colorless, air- and water- stable solids which can be sublimed at 1.3 Pa. $^1$H- and $^{13}$C-NMR spectra are highly symmetrical due to a fast exchange between the two possible conformers at room temperature (figure 12). By slow evaporation of solutions of BzTATC and PhTATC




*all-trans* *trans-trans-cis*

Figure 12: Conformers of RTATC

in hexane, colorless crystals could be obtained. **21** crystallizes with one independent molecule in the assymetrical unit (figure 13). **20** crystallizes with

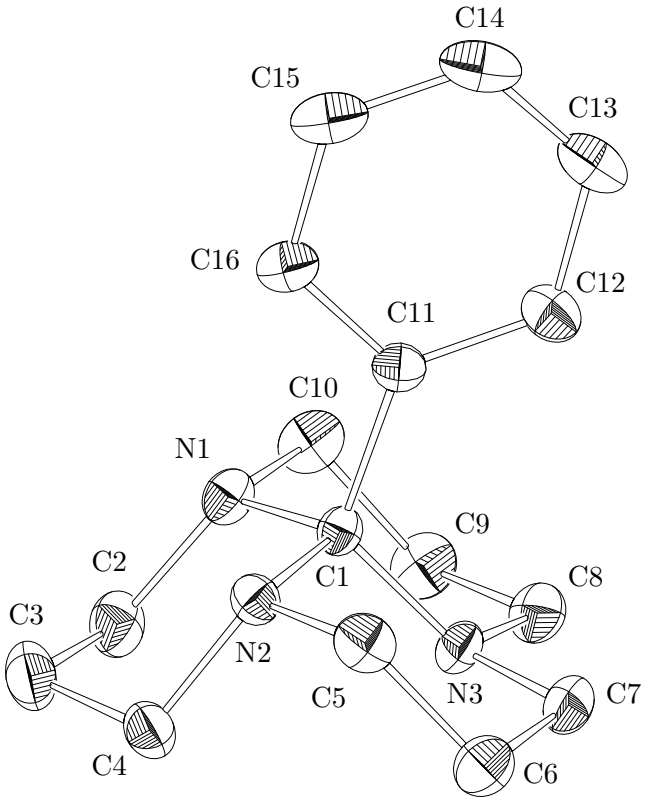



C1-C11 155.9(3), C11-C12 151.0(3), C(Ph)-C(Ph) 137.3(13), all other C-C 149.4(2), C1-N3 149.4(2), all other C-N 146.5(7); N3-C1-C11 112.0(2) N23-C1-C11 107.9(2), N-C1-N 109.7(3), C(*trans*-ring)-N-C1 113.2(8), C(*cis*-ring)-N-C1 115.7 (3), C1-C11-C12 116.8(2).

Figure 13: X-ray structure of BzTATC with selected bond length and angles

three independent molecules in the assymetrical unit, one of which is shown

in fig. 14. All of the three molecules are in the *trans-trans-cis*-conformation.



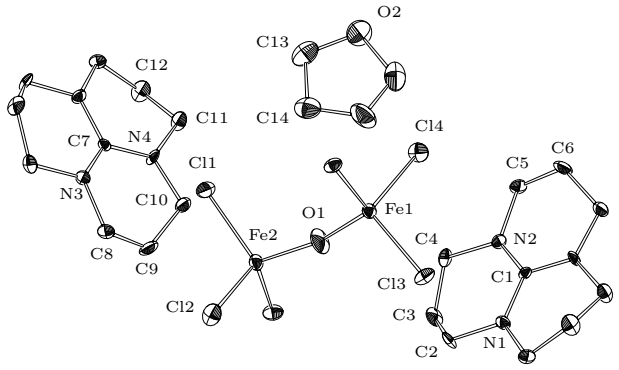

C1-C(Ph) 155.1(5), C(Ph)-C(Ph) 138.1(10), all other C-C 150.5(11), C1-N3 148.8(4), all other C-N 146.6(5); N3-C1-C(Ph) 117.4(5) N2-C1-C(Ph) 105.5(5), N-C1-N 109.4(4), C(*trans*-ring)-N-C1 111.2(6), C(*cis*-ring)-N-C1 116.1(7), C1-C11-C12 116.8(3),C1-C11-C16 125.4(3).

Figure 14: X-ray structure of one of the three independent molecules Ph-TATC with selected average bond length and angles

The structures of **20** and **21** are very similar to MeTATC **17** in the *trans-trans-cis*-conformation. The C-C-bonds from the central carbon atoms to the substituent R are longer than all the other C-C-bonds (155.1(5) pm in **20**, 155.9(3) pm in **21** and 154.0 pm in **17**). The C-N-bond between the two *trans*-rings is by 2-3 pm shorter than the other C-N-bonds. This is an indication for some strain in this bond. The substituent R is slightly bend away from this bond, so that the corresponding N-C-C(R) angle becomes slightly larger than the tetrahedral angle (117.5(5)° in **20**, 112.0(2)° in **21** and 113.5° in **17**).

### 2.1.2 Chemical Properties of RTATC

The oxidation of the central C-H bond in **16** has been thoroughly investigated by Wuest [22, 23]. It was shown that the tricyclic orthoamide undergoes a remarkably easy oxidation by a proton; when the $H^+$-tetrafluoroborate salt of **16** was heated to only 110 °C, the guanidinium salt was formed along with one mol equivalent of hydrogen gas. The central carbon-hydrogen bond of **16** must be extraordinarily reactive. So it was no surprise that in all attempts to make complexes of **16** with $FeCl_3$, which were successful with $R_3TAC$ [12], only the oxidation products could be isolated. Fig. 15 and fig. 16 show structures of two of the crystals which could be isolated from these attempts. The carbocation is in both cases easily identified by the short CN bond length and the planarity of the $N_3C^+$-unit. The Fe containing anions are in comparison with similar structures identified as $Fe^{III}$ in fig. 15 and $Fe^{II}$ in fig. 16. The product in fig. 15 has been obtained by oxidation of the product in fig. 16 probably by accidental intrusion of oxygen (see fig. 17).




Fe-O 173.9(14), Fe-Cl 220(4). N-$C^+$ 134.7(12), N-C-N 119.7

Figure 15: X-ray structure of $[HTATC]_2^+[Fe_2^{III}OCl_6]^{2-}(THF)$ with selected bond length and angles

Fe-$Cl_{terminal}$ 223.6(3), Fe-$\mu$-Cl 238.2(3). N-$C^+$ 134.1(14), N-C-N 119.6

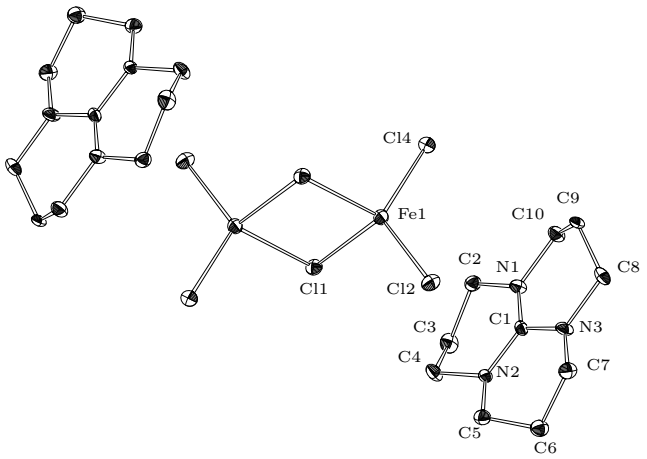



Figure 16: $[HTATC]_2^+[Fe_2^{II}Cl_6]^{2-}(Et_2O)$ with selected bond lengths and angles

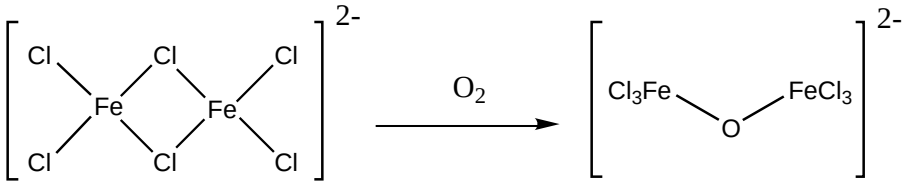
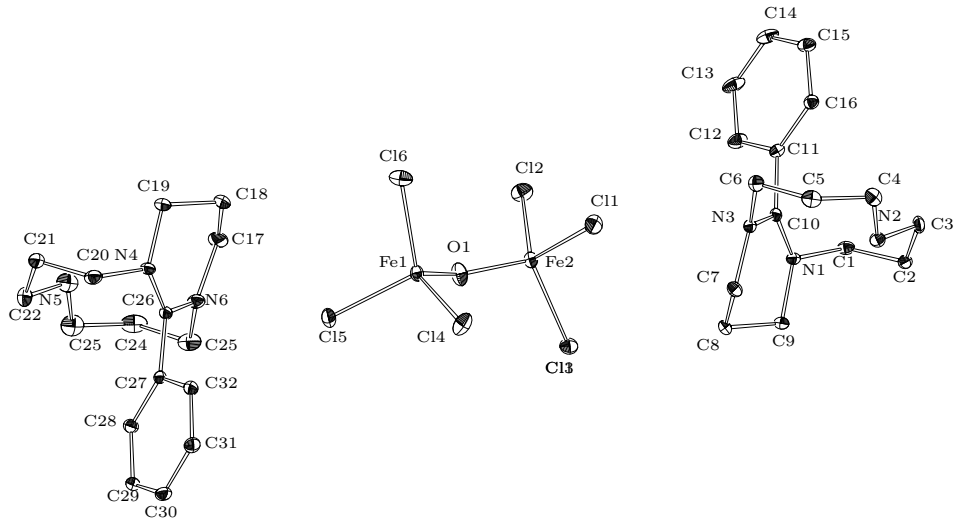



Figure 17: Oxiation of the $[Fe_2^{II}Cl_6]^{2-}$ anion (fig. 16)

### 2.1.3 Reaction of RTATC with Acid

The alkyl substituted derivates of HTATC were expected to be more stable against oxidation. Therefore another attempt was to prepare an $\eta^3$-complex of PhTATC and $FeCl_3$. However, during a period of several months in which the PhTATC$FeCl_3$ solution in ether was stored in a refrigerator to crystallize, water must have entered. A structure of the formed acid adducts can be seen in fig. 18. In another experiment a complexation of PhTATC with $VCl_3$ was attempted. However, after a very long time in the refrigerator, again only the product of the reaction with water could be isolated and crystallized. But in contrast to the reaction with Fe(III) which formed the isolated $[Fe_2OCl_6]^{2-}$ anion, this time the well coordinating $Cl^-$ as counter ion to the $[PhTATCH]^+$




Structure of $[\mathrm{PhTATC} + \mathrm{H}^+]_2(\mathrm{Fe_2OCl_6^{2-}})$; selected bond lengths [pm] and angles [°]: C2-N10 269(1), C10-N1 133.3(8), N1-C10-N3 123.2(3), N1-C10-C11 115.7(4)

Figure 18: X-ray structure of the acid adduct of $\mathrm{PhTATCFeCl_3}$

was hydrogen bridged to the cation. Figure 19 (p. 28) shows the differences in cations which result in the variation of the strength of the coordinating anion. This result is concurring with the results published by Wuest [22] about the reaction of HTATC with protons. By IR and NMR experiments it has been discovered, that the structure of the protonated HTATC depends strongly on the corresponding anion. With $\mathrm{Cl^-}$ as anion, HTATC as well as PhTATC are protonated at one nitrogen atom forming an ammonium ion. With $\mathrm{BF_4^-}$ instead of HTATC and $\mathrm{Fe_2OCl_6^{2-}}$ as weakly coordinating anion in the case of PhTATC, one of the central carbon-carbon bonds is nearly cleaved. Only a weak interaction remains with the resulting formamidinium ion (fig. 20 and 21). Both forms of the cation are, except for the one C-N-bond structurally, almost identical. Therefore this system might be a model for a case of bondstretch isomerism, an effect postulated by Chatt et al. [24] based

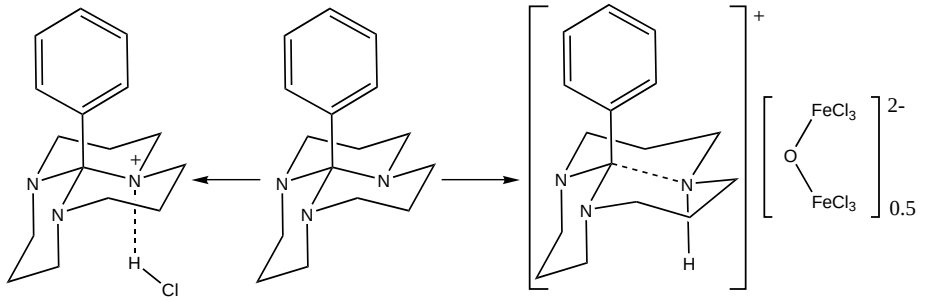



Figure 19: Acid adducts of PhTATC

on x-ray crystal structures and by Hoffman [25] based on theoretical studies. Since the rather accidentally formed $Fe_2OCl_6^{2-}$ anion is not a convenient starting material for further studies, it has been replaced with the large non-coordinating anion $((CF_3)_2C_6H_3)_4B^+$ with identical results [26]. Fig. 22 (p. 30) shows the corresponding x-ray crystal structure.

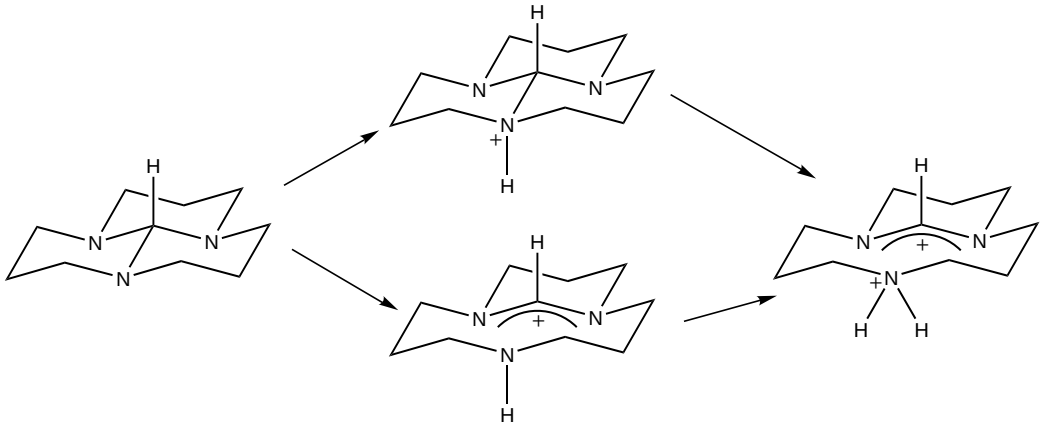
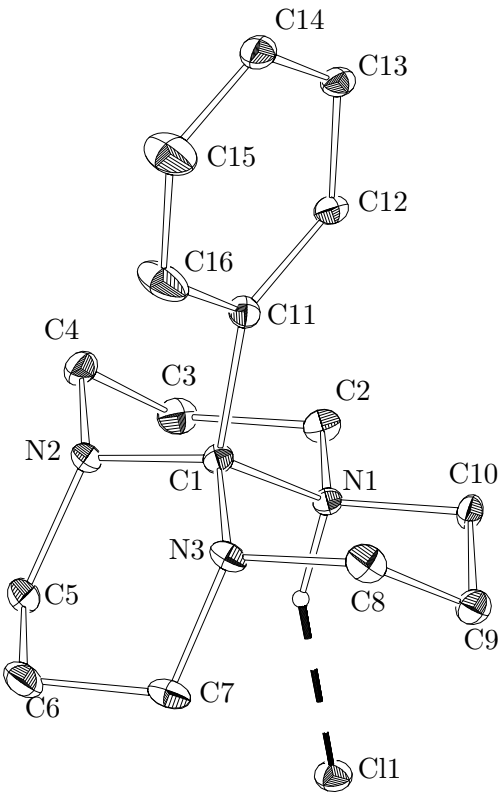



Figure 20: Acid adducts of HTATC




Cl1-N1 159.2(6), C1-N2 143.6(6) N2-C1-N3 113.0(4), N1-C1-C11 112.5(4)

Figure 21: X-ray crystal structure of the HCl-adduct of PhTATC with selected bond lengths [pm] and angles [°]

### 2.1.4 Complexes of RTATC

The first complexes of HTATC and MeTATC were molybdenum tricarbonyl complexes by Wong and Weisman [16]. The x-ray crystal structures and the carbonyl IR stretching frequencies of these complexes are consistent with the *fac*-$M(CO)_3$ structure, showing that the RTATC are indeed tridentate ligands.

Attempts to prepare analogous complexes using $CrCl_3 \cdot 3THF$ (fig. 23) gave quick results with correct elemental analyses and intact ligands indicated by IR spectra for RTATC with R = (H, Me, Bu, Ph, Bz, $CH_2Si(CH_3)_3$). One hint for an $\eta^3$-coordination of the RTATC-chromium complexes might

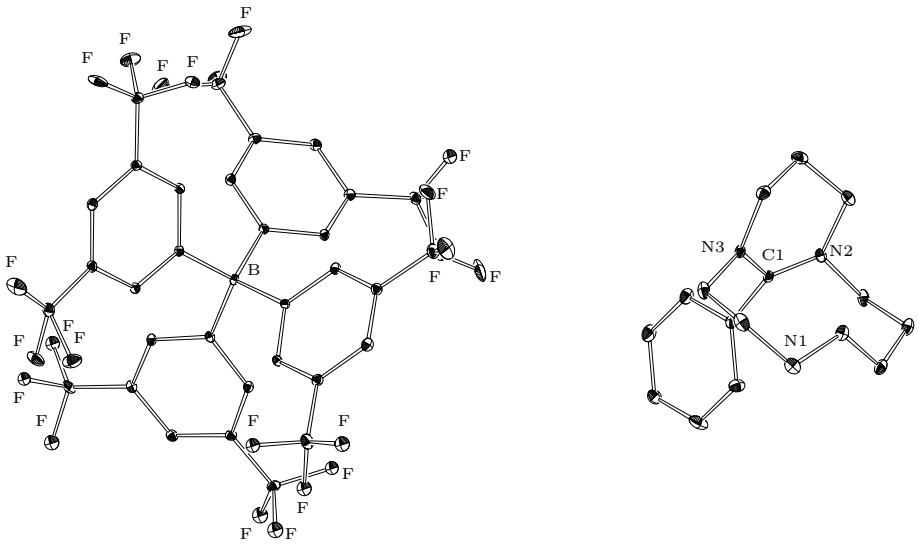



Figure 22: X-ray crystal structure of $[PhTATCH]^+[B(1,5\text{-}CF_3C_6H_3)_4]^-$ with cleaved C1-N1 bond.

be the observation that the $PhTATCCrCl_3$ complexes can be converted analogous to the $R_3TACCrCl_3$ complexes into $PhTATCCr(OTf)_3$ complexes by stirring a suspension of the chloride in pure trifluoromethansulfonic acid.

$$PhTATCCrCl_3 + 3TfOH \longrightarrow PhTATCCr(OTf)_3 + 3HCl$$

A free nitrogen atom in a possible $\eta^2$- or $\eta^1$-complex under the given con-

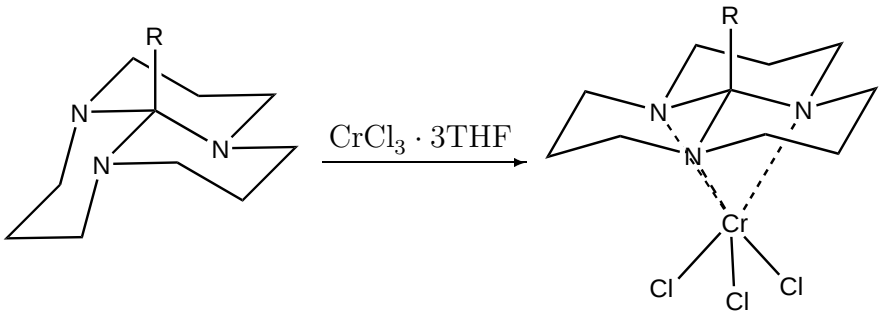
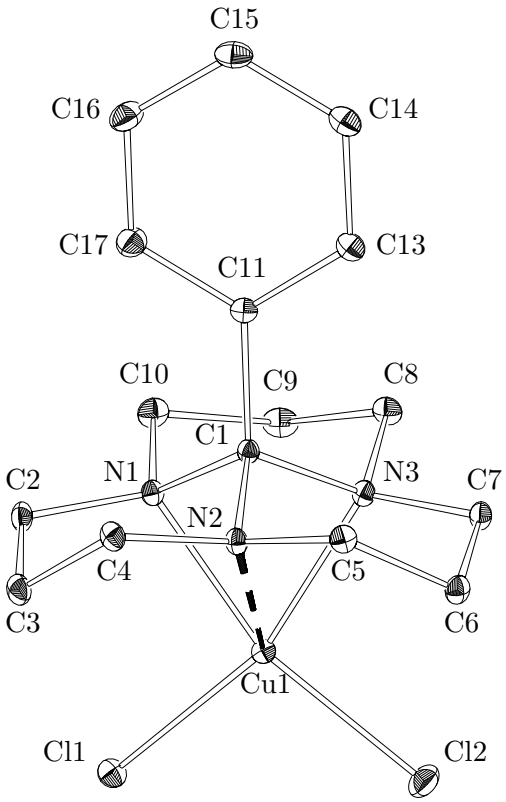



Figure 23: Synthesis of $R_3TACCrCl_3$ complexes.

ditions should have been protonated. In that case it should have been impossible to remove the acid *in vacuo* or by washing with pentane. If the ligand had been freed, it should have decomposed quickly in the strong acetic environment. However, this might be at best circumstantial evidence, but a good elemental analysis for C, H, N and S and an IR spectrum could be obtained, too. The extremely low solubility in all but the most polar solvents, in which these complexes quickly decompose, and their strong paramagnetism did not allow a more precise determination of their structure.

Some more information about the RTATC as ligand could be gathered by preparing the Cu(II)-complex of PhTATC from which an x-ray crystal structure could be obtained (fig. 24), and a zinc complex which provided information of the NMR-spectra of RTATC complexes (fig. 24, p. 32). The x-ray crystal structure of the Cu-complex shows a very interesting effect. With bond lengths of 206.9(2) pm and 207.3(2) pm between two of the nitrogen atoms and the copper atom, and with the copper atom located only 10 pm above the plane of the chlorine atoms and these two nitrogen atoms, the copper has a square planar coordination environment with an only $\eta^2$-coordinated PhTATC. The $\eta^2$-coordination is best seen in fig. 24 on page 32. The triangle shows the projection of the copper atom in the plane opened by the nitrogen atoms N1, N3, and N3 in correct scale. The distance of the copper atom from this plane is with 173.28 pm in the same range as the analogous distances in the triazacyclohexane copper complexes discussed later (see 2.2.1, p. 34). Though the third Cu-N distance is with 275.4(3) pm too long for a Cu-N bond and the position of the Cu atom is doubtless $\eta^2$, the ligand already has the all-*trans* conformation necessary for an $\eta^3$-complex.

Possibly, an agostic attraction between the Cu and the hydrogen of the $CH_2$-group in the position opposite to the third nitrogen might be dis-




Cu-N2 275.4(3), Cu-N1 207.3(2), Cu-N2 206.9(2), Cu-Cl1 220.98(12), Cu-Cl2 221.64(12), Cu-H9A 258(3), N1-Cu-N3 66.16(9), Cl1-Cu-Cl2 98.48(5)

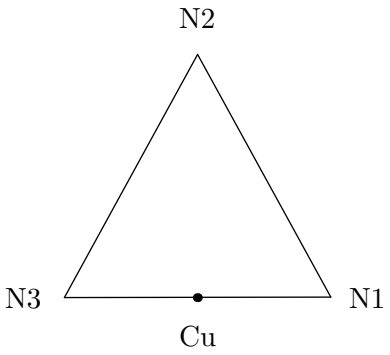



Figure 24: X-ray crystal structure of $PhTATCCuCl_2$ with selected bond length [pm] and angles [°] and the projection of the Cu atom in the N1-N2-N3 triangle

cussed. The Cu-(C-H) distance is with Cu-C9 = 285.6(4) pm and Cu-H9A = 258(3) pm similar to the bonding situation in the complexes [(Norbornadien)Cu(dien)]$^+$ (Cu-C = 278 pm; Cu-N = 208 − 225 pm [27]) and [Co(III)(dacoda)($SO_3$)] (Co-C = 252 pm; Co-N = 193 − 196 pm [28]) with agostic CH-groups. In the IR-spectra, however, no indication for a weakened C-H bond can be found. Additionally the propylene bridge is slightly bend out of the $N_3$-plane, indicating a repulsive rather than an attractive interaction.

The preparation of Zn complexes of BzTATC was of great interest, because of their diamagnetism and therefore the possibility of analysis by NMR-spectroscopy. The complexes were obtained according to the following equa-

tion:

$$ZnEt_2 + BzTATC + [Me_2NHPh]BF_4 \longrightarrow \mathbf{7} + Me_2NPh + C_2H_6 \uparrow$$

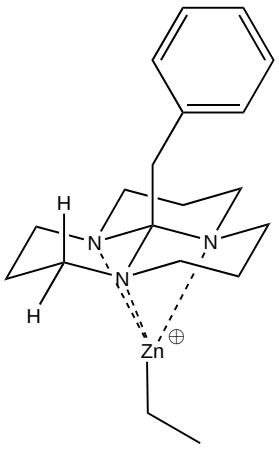



Figure 25: $[BzTATCZnEt]^+$ in **7**

The complexes are difficult to handle and very sensitive against water and air. Unfortunately no suitable crystals for x-ray crystal analysis could be obtained from $[BzTATCZnEt]^+BF_4$, but the diamagnetism of the complex allowed for the first time to get good $^1$H- and $^{13}$C-NMR spectra of coordinated RTATC. The spectra (p. 121) show signals for a highly symmetric BzTATC which is a sign for $\eta^3$-coordination.

## 2.2 Synthesis of 1,3,5-Trialkyl-1,3,5-triazacyclohexane Complexes $R_3TAC$

Parallel to the work on the $RTATCCrCl_3$ complexes, analogous work has been done using $R_3TAC$ as ligand:

$$R_3TAC + CrCl_3 \cdot 3THF \longrightarrow R_3TACCrCl_3 + 3\ THF$$

The Cr(III) complexes of $R_3TAC$ with small substituents (R = Me, $^i$Pr, Bz, cyclohexyl a. o.) are almost identical in melting point, color, solubility and stability to the $RTATCCrCl_3$ complexes. In other words the same problems

(paramagnetism, insolubility, for x-ray crystal structure analysis not suitable wool like crystal fibers) which were discussed for the RTATC chromium complexes are also true for the $R_3$TAC complexes.

For this reason and the formerly mentioned fact that hardly any information on $R_3$TAC complexes was available, some basic research had to be done for a better understanding of the coordination chemistry of $R_3$TAC. Therefore, and because of the similarity of RTATC and $R_3$TAC complexes, the same procedures used to examine the RTATC system were applied to the $R_3$TAC system, namely preparation and characterization of Zn, Fe, Cu complexes.

In this work only the Cu(I) and Cu(II) complexes of the triazacyclohexanes are discussed.

### 2.2.1 Cu(II)-complexes of Symmetrically Substituted $R_3$TAC

During the work on $R_3$TAC complexes of Cu(II) x-ray crystals structures of $^{i}Pr_3TACCuCl_2$ and "$Me_3TACCuCl_2$" **8** could be obtained by R. Köhn [29] (for an analogous chiral $R_3$TACCu(II) complex see [30]). The $^{i}Pr_3TACCuCl_2$ is a monomer with a nearly $\eta^3$-coordinated $^{i}Pr_3$TAC (Cu-N 203.8(1), 206.3(4) and 224.6(4) pm)). The structure of the $Me_3$TAC complex is quite different (fig 26). Due to the smaller nitrogen substituents two complexes are associated by two chlorine bridges forming a dimer. The paramagnetism of this compound made it difficult to get useful $^{1}$H- or $^{13}$C-NMR spectra. The $^{2}$H-spectra of ring deuterated **65** in $MeNO_2$ is difficult to interpret due to the low solubility of **65**, but shows two sets of signals at $\delta = 2.8$, $\delta = 7.8$, $\delta = 71$ and 30. This may indicate a monomer-dimer equilibrium in $MeNO_2$ [29]. To backup such interpretation several attempts were made to grow crystals of monomeric **65** which should allow to investigate the equilibrium. Unfortu-

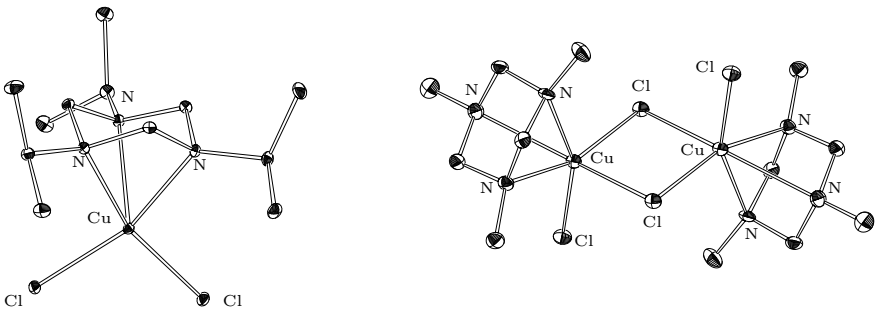



Figure 26: X-ray crystal structures of $^{i}Pr_3TACCuCl_2$ and $(Me_3TACCuCl_2)_2$ [29]

nately it was not yet possible to get a $Me_3TACCuCl_2$ structure analogous to $^{i}Pr_3TACCuCl_2$. However, the attempt to prevent the dimerisation by a very quick precipitation of the formed complex by pouring a saturated solution of $CuCl_2$ in ethanol into a large excess of $Me_3TAC$ under rapid stirring resulted in a bright yellow solid. This compound can be crystallized from toluene and gives the x-ray crystal structure in fig. 27.

Cu-N1 201.9(4), Cu-N2 251.0(4), Cu-N3 262.1(4), Cu-N4 201.9(4), Cu-Cl1 231.96(13), Cu-Cl2 233.37(13), Cl1-Cu-Cl2 115.45

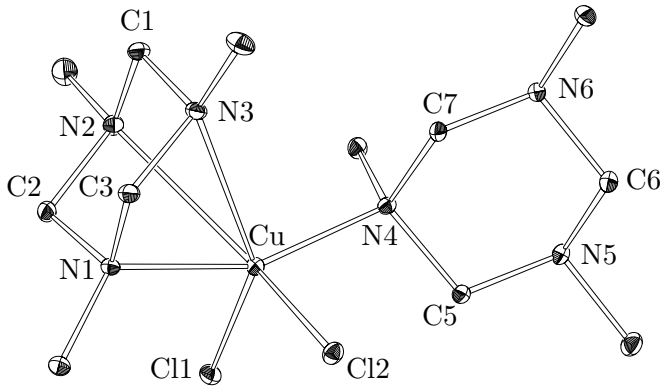



Figure 27: X-ray structure of $(Me_3TAC)_2CuCl_2$ with selected bond lengths [pm] and angles [°]

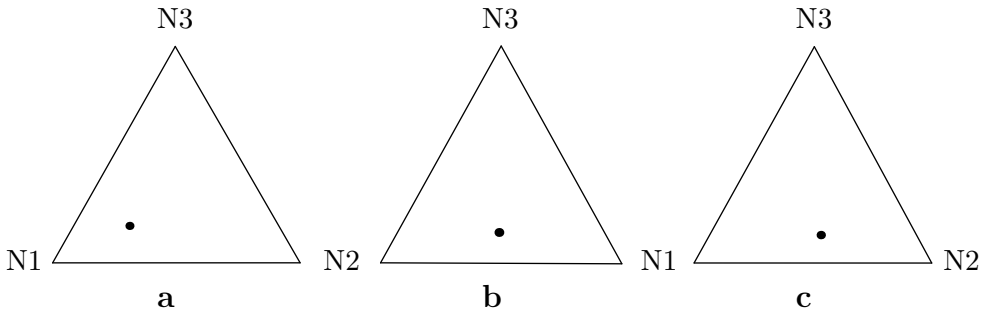



Figure 28: Relative positions of the copper atom under the N(1)-N(2)-N(3)-nitrogen planes of $(Me_3TAC)_2CuCl_2$ (**a**), $^{i}Pr_3TACCuCl_2$ (**b**) and $(Me_3TACCuCl_2)_2$ (**c**)

Now the Cu(II)-atom is coordinated to two $Me_3TAC$ ligands. When the Cu-N bond lengths of the dimer are compared with the corresponding Cu-N bond lengths of this monomer, it shows that two of the bonds are almost in the same range (Cu-N monomer:dimer = 201.9(4):206.4(8) pm and 262.4(4):259.7(12) pm). The third "$\eta^3$"-distance increased by about 36 pm from Cu-N = 215.1(10) pm to Cu-N = 251.0(4) pm. The Cu-N bond length of the $\eta^1$-coordinated $Me_3TAC$ is 202.8 pm. Since two of the C-N bond lengths are quite long the question arises, whether this complex really is an $\eta^1/\eta^3$-complex or whether it is better described as $\eta^1/\eta^1$-complex. Figure 28 shows the projection of the Cu atom onto the plane opened by the nitrogen atoms N(1)-N(2)-N(3) in correct scale. The point is the position of the copper atom below this plane. The three nitrogen atoms form nearly a perfect isosceles triangle (angles: 60.05, 60.44 and 59.51 °). A pure $\eta^3$-coordinated atom would lie in the center of the triangle. Since fig. 28 alone does not allow to decide what coordination type describes the structure better, another criterion had to be used.

The common coordination geometry for Cu(II) with $C_N$ 4 ($\eta^1/\eta^1$) is square planar and with $C_N$ 6 ($\eta^1/\eta^3$) distorted octahedral. Table 1 shows that the four short bonds do not form a square but are part of an octahedron with the two remaining nitrogen atoms occupying two cis positions (see fig 29). The two long Cu-N bonds are stereochemically active, i. e. the short Cu-N and Cu-Cl bonds are bend away from the ideal quadratic-planar configuration to a more tetrahedral configuration.

In a square planar complex, there are three possible d-d transitions: $d_{xy}(d_{yz}) \longrightarrow d_{x^2-y^2}(\nu_1)$; $d_{z^2} \longrightarrow d_{x^2-y^2}(\nu_2)$; $d_{xy} \longrightarrow d_{x^2-y^2}(\nu_3)$. Fig. 30 shows qualitatively the change of the orbitals during the transition from a complex with coordination number four (tetrahedral, square planar) to a complex with coordination number six (octahedral). On the right side of fig. 30 can be seen, that the more the square planar coordination changes to square bipyramidal coordination and finally to an octahedral complex through the approach to two more bonds, the more the value of $\nu_1$ should decrease and become equal to $\nu_2$. The value of $\nu_3$ should also decrease, and finally vanish in an ideal octahedral complex, since then the $e_g$ orbitals are all degenerated. This would also be true when the starting structure is not square planar, but tetrahedral and the intermediate is not square bipyramidal, but has a structure like the $(Me_3TAC)_2CuCl_2$ in fig. 29. So the color change from deep green of the complexes in fig. 26 to bright yellow in case of $(Me_3TAC)_2CuCl_2$ can be explained by deviation from the ideal square

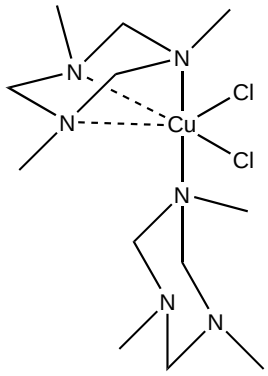



Figure 29: $(Me_3TAC)_2CuCl_2$

planar or tetrahedral geometry of the complex in direction of an octahedral geometry.

Another result of this deviation is the ease the Cu(II) can be reduced to Cu(I) in this complex as it is observed later. It is the same principle, promotion of redox processes by strained configurations through appropriate ligands, which can be observed in several systems in nature [31, 32]. Re-

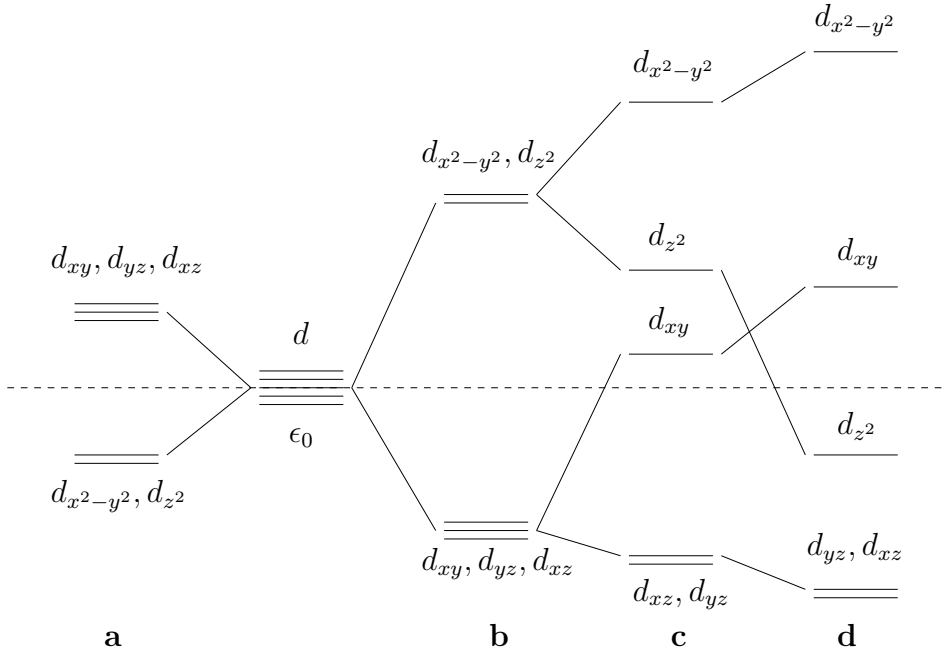



Figure 30: **a** tetrahedral field, **b** octahedral field, **c** square bipyramidal field. **d** square planar field

garding this observation it is surely valid to speak in case of **9** as of an $\eta^1/\eta^3$-complex. The distance of the Cu atom from the plane opened by the nitrogen atoms N(1)-N(3) is 188.5 pm. This distance is about 12 pm longer than the distance from the equivalent plane in the dimer (176.3 pm). **9** is in solution not only very air sensitive, but probably undergoes under certain conditions internal rearrangements. Several attempts to recrystallize $(Me_3TAC)_2CuCl_2$ failed until pure $Me_3TAC$ was used as solvent. It was observed, that after

Cu1-Cu2 292.1(7), Cu1-Cl1 210.9(7), Cu1-Cl2 211.5(7), Cu2-Cl3 211.5(9), Cu2-Cl4 211.4(6), Cu3-Cl5 227.1(7), Cl1-Cu1-Cl2 171.4(5), Cl1-Cu1-Cu2-Cl3 87.7(9)

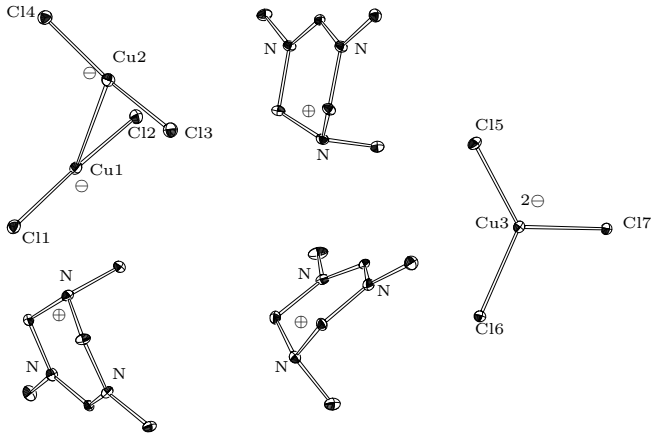



Figure 31: A section of the x-ray structure of the product of the reduction of $(Me_3TAC)_2CuCl_2$ with $Me_3TAC$ with selected bond lengths [pm] and angles [°]

the recrystallization the mother liquor, normally a water clear, colorless liquid, turned quickly green upon exposure to the slightest traces of oxygen. Under exclusion of free oxygen the green solution consumes the oxygen and turns colorless again within several days. This can be repeated several times. After several of these "oxidation-reduction" cycles colorless crystals start to grow in the mixture. Fig. 31 shows the x-ray crystal structure which could be obtained from these crystals. Obviously the $Me_3TAC$ was able to reduce

| | | | |
|---|---|---|---|
| **Cl(1)-Cu-Cl(2)** | **115.45** | **Cl(1)-Cu-N(1)** | **94.92** |
| **Cl(2)-Cu-N(1)** | **94.18** | **Cl(2)-Cu-N(4)** | **98.66** |
| **Cl(1)-Cu-N(4)** | **95.63** | **N(1)-Cu-N(4)** | **157.95** |
| Cl(1)-Cu-N(2) | 143.97 | Cl(2)-Cu-N(2) | 93.51 |
| N(1)-Cu-N(2) | 60.27 | N(2)-Cu-N(4) | 100.91 |

Table 1: Bond angles [°] between the short bonds to Cu in **9** (bold) and their angle to one of the longer bonds Cu-N2

the Cu(II) to Cu(I). The mechanism of this reaction is not clear yet, but it is well known that triazacyclohexanes can be oxidized according to fig. 32 (see also [33]). Nevertheless, irrespective of the mechanism, the struc-

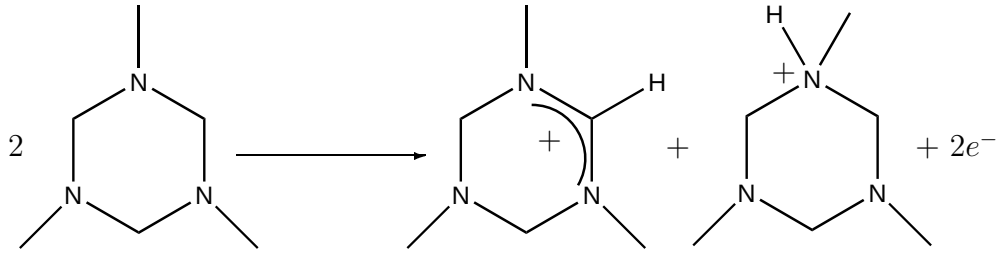



Figure 32: Oxidation of triazacyclohexanes

tures of the anions are very interesting. The crystals consist of six cations of the oxidized $Me_3TAC$ ($[oxMe_3TAC]^+$, see fig. 32) and two sorts of Cu(I) containing anions: $(oxMe_3TAC)_6(CuCl_3)_2(Cu_2Cl_4)$ **10**. Though trigonal planar $[CuCl_3]^{2-}$ seems to be quite rare, at least two more examples of this structure could be found [34, 35] in literature. Much more interesting is the structure of the $[Cu_2Cl_4]^{2-}$ anion. Attractive interactions between formally closed-shell metal centers ($s^2$ or $d^{10}$) are well documented [36]. Especially for Au(I) many examples can be found, so that the special term *aurophilicity* has been coined to describe this special kind of metal-metal attractive interaction [37]. The question whether a similar *metallophilicity* [38] exists for copper or silver, is still a matter of controversy [39]. Metallophilic effects are easily blurred by effects exerted by a bridging ligand architecture, and hence examples of ligand-unsupported metal-metal interactions are of great importance in this discussion. They are, however, notoriously scarce for silver [40] and especially for copper [41]. One example is a trinuclear species $[CuL]_3$ (HL= 2-[3(5)-pyrazoyl]pyridine)(fig. 33). It crystallizes as a dimer showing

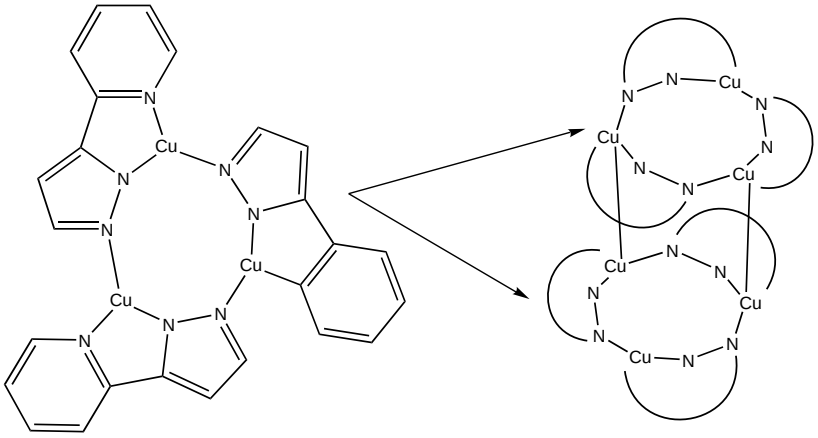


Figure 33: $[Cu_3(2\text{-}(3(5)\text{-}pz)py)_3]$ and dimer [41].

two close metal-metal contacts between the two associated trinuclear units in the absence of any supporting bridging ligation [d(Cu-Cu) = 290.5(3) pm] [41]. Another example is reported by Siemeling [39].

In the $[CuL]^+[CuCl_2]^-$ **11** (L = 1,1'-bis(2-pyridyl)octamethylferrocene) the almost linear $[CuCl_2]$ unit is approximately perpendicular to the N-Cu-N unit (fig 34) with a Cu-Cu distance of 281.0(2) pm and the torsion angles are 85.5 ° and 89.4 ° [39]. Bénard and Poblet [42] did a theoretical analysis of the ligand-unsupported Cu(I)-Cu(I) interaction in the complex in fig. 34. According to them density functional theory calculations explain the short

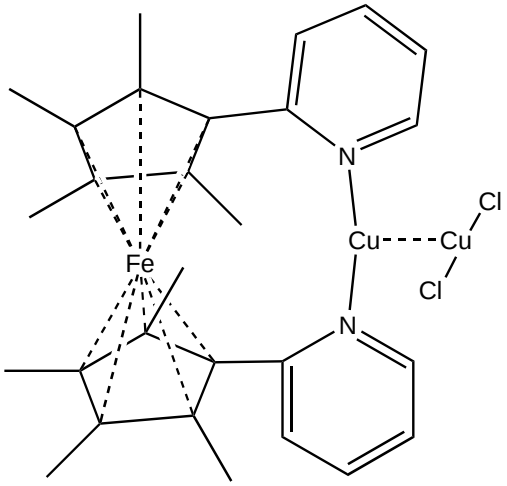


Figure 34: Simeling complex [39]

Cu(I)-Cu(I) contact in **11** by a strong electrostatic attraction between the two moieties and rule out the initially suggested metallophilic interaction. An electrostatic attraction is certainly ruled out in the $[Cu_2Cl_4]^{2-}$ anion. In this anion the 1,1'-bis(2-pyridyl)octamethylferrocene-$Cu^+$ unit is replaced by a second $[CuCl_2]^-$ unit. The angles in both compounds are almost identical. The Cl(1)-Cu(1)-Cl(2) and the Cl(4)-Cu(2)-Cl(3) are 171.46(11) ° and 164.98(11) °. The Cl-Cu-Cu-Cl dihedral angles are about 90 °. The Cu-Cu distance is with 292.17(17) pm slightly longer, but in the range of known Cu(I)-Cu(I) distances of comparable compounds. So with **10** a system might have been found on which possible *cuprophilicity* effects might be studied without disturbing influences of unsymmetrical ligand substitutions and which is even strong enough to overcome the electrostatic repulsion between the anions. However, nothing can be said about possible packing effects in the crystal since no effort has been taken yet to find the anion in solution.

### 2.2.2 Cu(I)-complexes of Symmetrically Substituted $R_3TAC$

The Cu(I) complexes of $R_3TAC$ are available by treatment of $[Cu(CH_3CN)_4]X$ (X= $BF_4$, $PF_6$) with $R_3TAC$ (R = $^i$Pr, Bz, cyclohexyl) in $CH_2Cl_2$:

$$R_3TAC + [Cu(CH_3CN)_4]BF_4 \longrightarrow [(R_3TAC)Cu(CH_3CN)]BF_4 + 3\ CH_3CN$$

These complexes are pure white and extremely air sensitive solids. By replacement of the acetonitrile ligand with $PPh_3$ the much more stable $[(R_3TAC)$- $Cu(PPh_3)]X$ can be obtained. All attempts to wash $[(R_3TAC)Cu(CH_3CN)]X$ with THF resulted in an exchange of the acetonitrile, giving $[(R_3TAC)Cu(THF)]X$. These complexes are diamagnetic and therefore easily to examine by NMR-spectroscopy. Especially the $^1$H-NMR spectra are very characteristic for coordinated $R_3TAC$ ligands. While in the

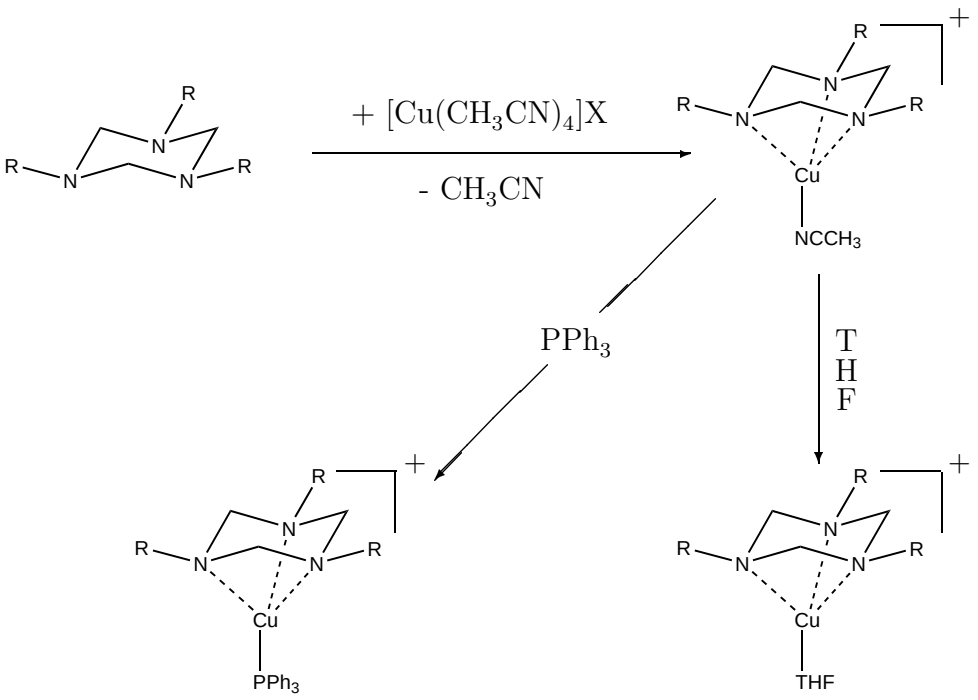



Figure 35: Synthesis of [($R_3$TAC)CuL]X complexes. L = $CH_3CN$, $PPh_3$, THF; X = $BF_4$, $PF_6$

free ligand the ring protons are indistinguishable and show a broad signal near coalescence at about 3.2 ppm at room temperature, their signal is split in the Cu(I)-complexes into two sharp doublets, indicating a $\eta^3$-coordinated and symmetrical environment, for the endo- and exo-protons. Figure 36 is an example of the $^1$H-NMR spectrum of $^i$Pr$_3$TAC and in figure 37 the $^1$H-NMR spectrum of the Cu(I) complex of the same ligand with the splitting of the ring protons. The signals of the benzyl substituted complex are slightly broader, possibly indicating a less symmetrical substitution. The $^{31}$P-NMR spectra show a signal in the typical area between 9 and 12 ppm for Cu(I)-$PPh_3$ complexes ([(HB(3, 5- $Me_2$pz)$_3$)Cu($PPh_3$)]: 11.87 ppm [43]). The

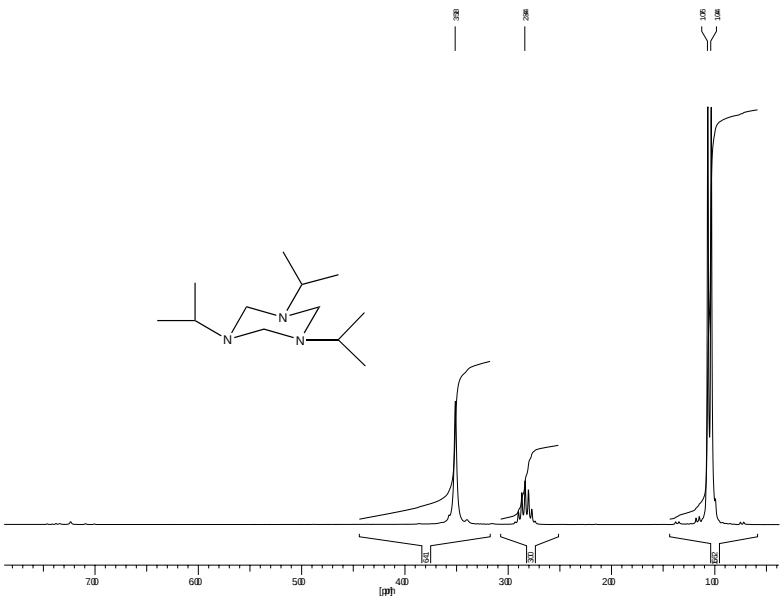



Figure 36: $^{1}$H-NMR spectrum of $^{i}Pr_3TAC$

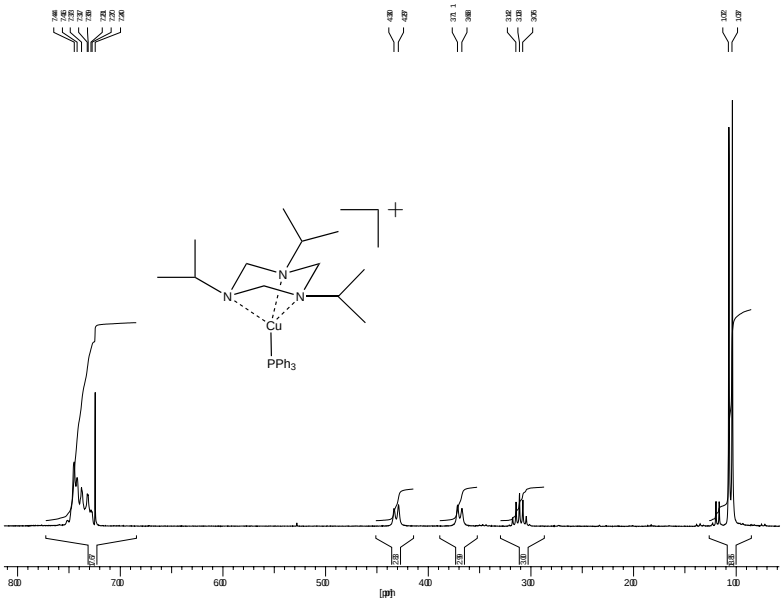


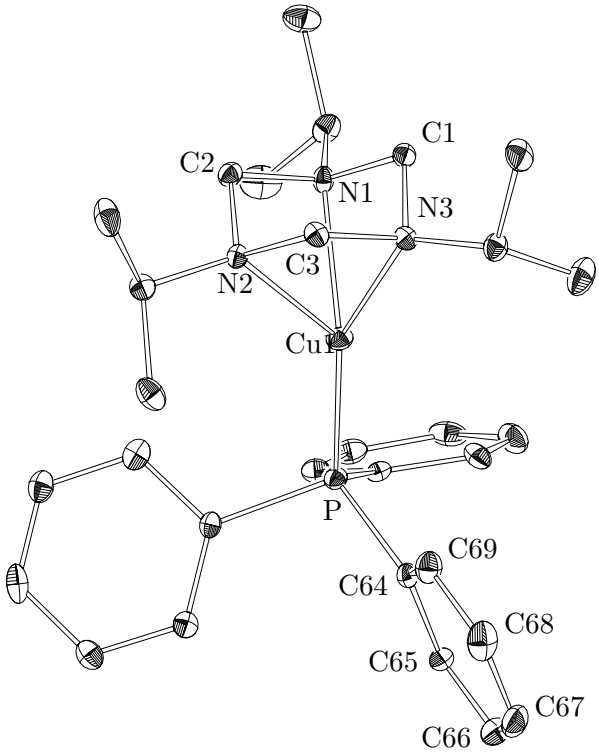

Figure 37: $^{1}$H-NMR spectrum of $[(^{i}Pr_3TAC)Cu(PPh_3)]BF_4$

$^{13}$C-NMR spectra are also consistent with the data from other Cu(I)-$PPh_3$ complexes [44, 45]. In $^{19}$F-NMR spectra one signal for a free, symmetrical $BF_4^-$ can be found.

The IR spectra of these complexes show the typical absorption bands for $R_3$TAC ligands. Though the area around 500 $cm^{-1}$ is clearly dominated by the $PPh_3$ signals, the signals typical for an $\eta^3$-coordination could be found by comparison of several spectra including one with in the ring positions deuterated $Bz_3$TAC. These characteristic bands were about 10 $cm^{-1}$ shifted to lower wave number against the position of the equivalent bands of the Cr(III) complexes [46]. Therefore the bond of the $R_3$TAC in the Cu(I)-complexes must be weaker than in the Cr(III)-complexes [12]. The IR-spectra, too, indicate, that unlike in the $Cy_3$TAC (Cy = cyclohexyl) and $^{i}Pr_3$TAC complexes the $Bz_3$TAC ligand is in the Cu(I)-complex unsymmetrically bonded. The IR-spectrum of the $[(Bz_3TAC)Cu(PPh_3)]BF_4$ complex shows a signal at 504 and 479 cm (447 and 428 cm for the deuterated compound), while the other complexes show only one signal in this area.

By slow diffusion of toluene into a solution of the complex in $CH_2Cl_2$ colorless crystals of $[(^{i}Pr_3TAC)Cu(PPh_3)]BF_4 \cdot 0.5\,(C_7H_8)$ and $[(Bz_3TAC)$-$Cu(PPh_3)]BF_4$ could be obtained.

The structure of $[(^{i}Pr_3TAC)Cu(PPh_3)]BF_4$ **12** contains two independent cations. Figure 38 shows one of these. Both structures show approximately tetrahedral coordination. In one of the structures the $^{i}Pr_3$TAC is roughly $\eta^3$-coordinated (Cu-N = 217.6(5), 220.1(5) and 220.2(4) pm) while in the other cation one of the Cu-N bond length with 215.0(4) is clearly shorter than the other two distances with 223.4(4) and 223.7(4) pm. One of the ring $CH_2$-groups is found to be closer to the Cu-atom (265.2(5) pm), but no further indication for an agostic effect could be found. The structure




Cu1-N1 217.6(5), Cu1-N2 220.1(5), Cu1-N3 220.2(4), Cu1-P1 212.4(2), P1-C64 181.2(6), N1-Cu1-N2 64.3(2), P1-Cu1-N2 140.66(13)

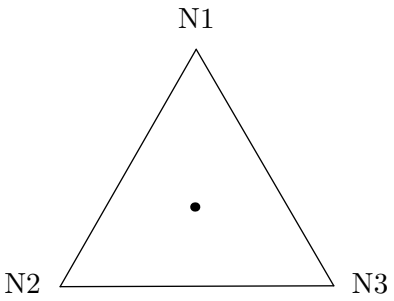



Figure 38: X-ray structure of one of two independent cations of [$^{i}$Pr$_3$TACCuPPh$_3$]BF$_4$ with selected bond lengths [pm] and angles [°] and a projection of the copper atom in the by the three nitrogen atoms N1, N2, and N3 opened plane in correct scale

of the [(Bz$_3$TAC)Cu(PPh$_3$)]BF$_4$ **13** is quite different from the structures of the $^{i}$Pr$_3$TAC complex. The Cu-N distances range from 215.0(4) pm and 221.0(2) pm to 244.6(3) pm. All three benzyl groups are oriented to the metal. However, a bonding interaction with the Cu-atom can be ruled out. With the shortest Cu-C distance of 349 pm it definitely is too long. However, again one of the ring CH$_2$-groups is quite close to the Cu-atom (260.0(3) pm). And unlike the other copper complexes with similarly short Cu-CH$_2$ distances, the IR-spectrum of **13** shows a strong C-H valence band at 2786 cm$^{-1}$, indicating a noticeably weakened bond. This band shifts in the ring deuterated

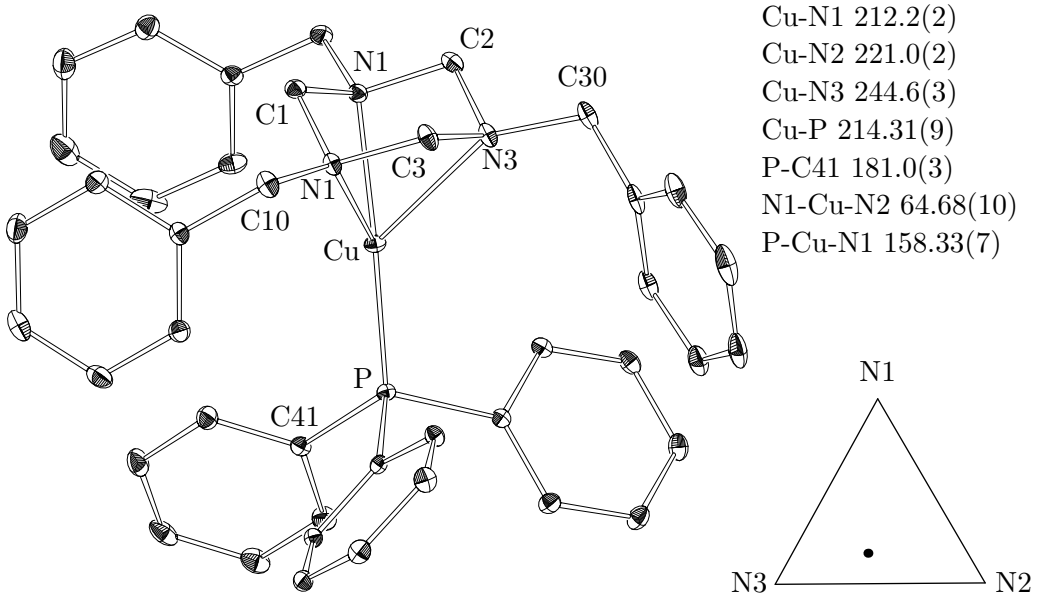



Figure 39: X-ray structure of $[Bz_3TACCuPPh_3]BF_4$ with selected bond lengths [pm] and angles [°] and the projection of the copper atom in the by the three nitrogen atoms N1, N2, and N3 opened plane in correct scale.

compound to 2026 $cm^{-1}$. The strong difference in intensity in comparison to the "non-agostic" C-D bands at 2233, 2219 and 2075 $cm^{-1}$ indicate, that in **13** an agostic attraction may actually exist.

The bond lengths to the phosphanes are in both $[(R_3TAC)Cu(I)(PPh_3)]^+$ complexes almost equal (214.31(9) in **13**, 212.4(2) and 213.7(2) pm in **12**). This is slightly shorter than in other Cu(I)-$PPh_3$ complexes ($215 - 230$ pm). When the UV/Vis-spectra of $Bz_3TACCrBz_3$ and $Cy_3TACCrBz_3$ are compared with with the spectra of $[Cp^*CrBz_3]^-$, it shows that $Cp^*$ and $R_3TAC$ have a similar ligand field strength (as far as this model is applicable with these sort of complexes). Comparison of x-ray crystal structures of both complex classes show that there are many structural similarities, too [12].

A thorough discussion of the analogous Cp-Cu structures is difficult, since there are only three x-ray crystal structures of CpCu-complexes known, which are all Cu(I)-complexes [47, 48, 49]. Nevertheless, table 2 (p. 48) shows, that

| | Complex | Ring-Cu | Cu-P |
|---|---|---|---|
| TATC: | $PhTATCCuCl_2$ | 173.28 | |
| Cu(II): | $^{i}Pr_3TACCuCl_2$ | 172.4 | |
| | $(Me_3TACCuCl_2)_2$ | 176.3 | |
| | $(Me_3TAC)_2CuCl_2$ | 188.5 | |
| Cu(I): | $[Bz_3TACCuPPh_3]BF_4$ | 179.0 | 214.31(9) |
| | $[^{i}Pr_3TACCuPPh_3]BF_4$ | 177.2 | 212.4(2) |
| CpCu: | $CpCuPPh_3$ | 186.4 | 213.5(2) |
| | $CpCuPEt_3$ | 190.5 | 213.5(9) |

Table 2: Perpendicular ring-Cu distances and Cu-P distances (if applicable) of several TATC, TAC and Cp copper complexes

the structural differences between CpCu- and $R_3TAC$/RTATCCu-complexes are not particularly large either. The hapticity of the $R_3TACCu$-complexes can steadily vary from $\eta^1$ to $\eta^3$ which reminds of the 'ring slippage' of the Cp-complexes. With NMR spectroscopic experiments (spin saturation transfer) Mountford could prove the rotation of the $Me_3TAC$ on titanium complexes and determine the activation energy of this process to $\Delta G^{\ddagger}= 62.9 \pm 0.5$ kJmol$^{-1}$ at 292 K [11] and is even higher in complexes of $R_3TAC$ with sterical demanding substituents. Though the energy is much higher than in an analogous metallocene, it still shows that properties found in Cp-complexes can also be expected in $R_3TAC$ complexes.

## 2.3 Synthesis and Characterization of Unsymmetrically Substituted Triazacyclohexanes $R_2R'TAC$

Unsymmetrically substituted triazacyclohexanes are triazacyclohexanes with two or three different substituted nitrogen atoms. At the beginning of this work only very few examples for such TACs were available (see fig. 8 on p. 18). Since the synthetic routes for these TACs are not adaptable for a greater range of different unsymmetrically substituted TAC, new synthetic routes had to be developed.

### 2.3.1 Synthesis of Unsymmetrically Substituted $R_2R'TAC$

The first, most obvious attempt to prepare these compounds was simply to let a mixture of primary amines react with formaldehyde and hope for an at least statistical distribution of the possible products. Further, in case of satisfying results with this method, a manageable method to separate the products in this mixture should be found.

Unfortunately the rate of the reaction between a primary amine and formaldehyde depends more strongly on the amine than expected. In an NMR-experiment formaldehyde was added successively in small portions to a mixture of methylamine and benzylamine. The resulting $^1$H-NMR spectra clearly showed that the benzylamine only began to react with the formaldehyde when all the methylamine was used up. This was conform to the observations made in several experiments with different amines and solvents where reproducible yields near 0% of $R'R_2TAC$ were observed.

Finally, after a long row of experiments with varying solvents, temperatures, concentrations and amine ratios, $R'R_2TAC$ yields of up to 60% have been found. These results were obtained with ethanol as solvent. The ratio

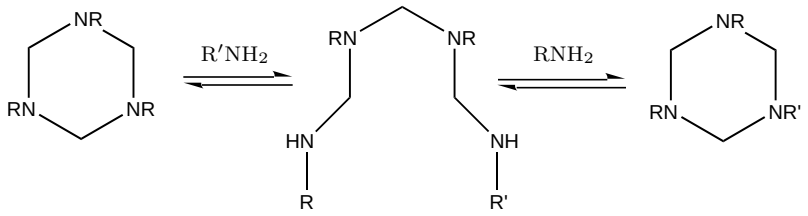



Figure 40: Equilibria in $R_3$TAC synthesis

of the two amines in this mixture was about 100:1 and the concentration of the mixture in ethanol was between 0.5 and 1.2 $moll^{-1}$. Lower concentrations give even better results, but the absolute yields become unacceptable low.

For the special case of $R'R_2$TAC with R = Me or R = Et a second method was found by shifting the equilibrium in fig. 40 at 130 °C through removal of the more volatile amines $MeNH_2$ or $EtNH_2$:

$$Me_3TAC + R'NH_2 \longrightarrow R'Me_2TAC + MeNH_2 \uparrow$$

### 2.3.2 Separation of Unsymmetrically Substituted $R_2R'$TAC

With both methods, mixtures with a large excess of symmetrical TAC and only a few percent of the desired $R'R_2$TAC are obtained. Fortunately it proved that other combinations $R'_3$TAC and $R'_2$RTAC are negligible. However, the equilibrium in fig. 40, is only one of a row of observed equilibria in the chemistry of triazacyclohexanes (fig. 41) [2]. These equilibria are of course of no consequence for symmetrical $R_3$TAC, but it could have meant that unsymmetrically substituted triazacyclohexanes are not stable and undergo internal rearrangements, making it impossible to isolate them. Luckily most $R'R_2$TAC are meta stable at room temperature. In the absence of acids and water they even tolerate temperatures of about $80 - 90$ °C. So after drying

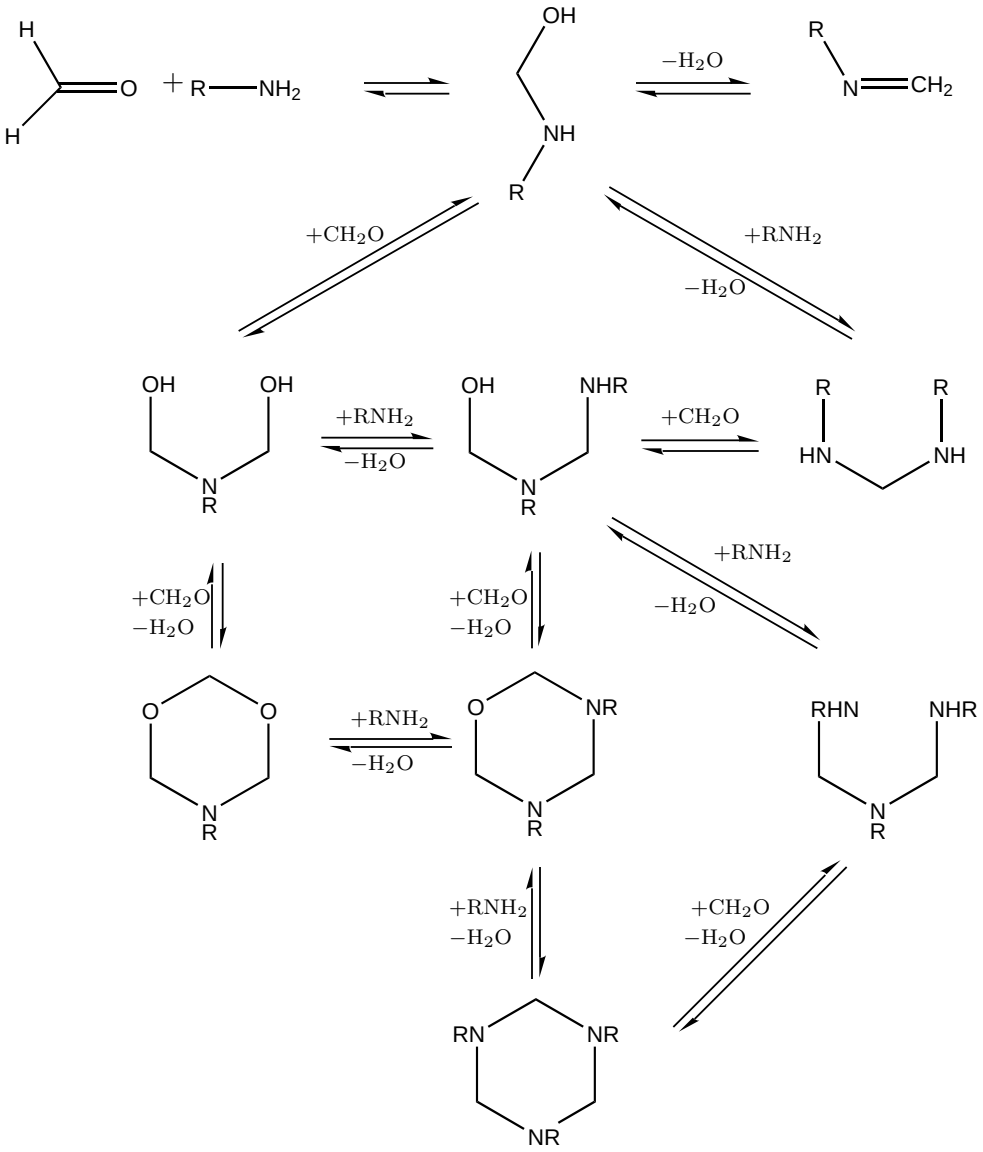



Figure 41: Equilibria in $R_3$TAC synthesis

with sodium some of the small R′$R_2$TAC (R = Me, Et, Bu, $^{i}$Pr; R' = Bz, $^{t}$Bu) can be distilled in vacuum. Larger R′$R_2$TAC, like ($C_8H_{17}$)$Et_2$TAC can be purified with standard methods (column chromatography, recrystallization). The only exception where adapted methods had to be developed were triazacyclohexanes with an OH-functionalized substituent (see below).

### 2.3.3 R′$R_2$TAC (R', R = aliphatic or aromatic) with no Functional Groups

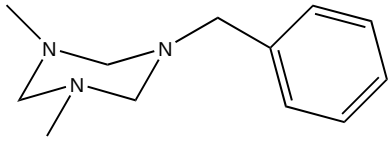



Figure 42: ($CH_3$)$_2$BzTAC

Basically three different classes of unsymmetrically substituted triazacyclohexanes were of interest in this work. Figure 29 shows an example of the most basic class. All three substituents are aliphatic or aromatic. None of the substituents carries a functional group. But they allowed to investigate the differences between symmetrically and unsymmetrically substituted TACs, their stability against acids and higher temperatures, and their spectroscopical properties.

### 2.3.4 R′$R_2$TAC with one Functionalized Substituent

Although the literature dealing with triazacyclohexanes is extensive and triazacyclohexanes bearing functional groups (e.g. hydroxyl, allyl, nitro, nitrile, esters, amides, pyridyl) [2], studies of coordination chemistry of this family of ligands has been limited to 1,3,5-triazacyclohexanes with simple substituents (e.g. Me, $^{t}$Bu, $^{i}$Pr, Bz). Recently, Baker and coworkers synthesized a number of chromium complexes of triazacyclohexanes bearing three hydroxy groups [50]. However, in most cases unsymmetrically substituted triazacyclohexanes

bearing only one functional group X (X= -OH, -CN, -$NH_2$; see fig. 43 are much more interesting.

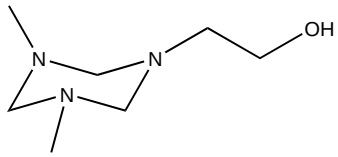



Figure 43: $(CH_3)_2$TACEtOH

There are several reasons to prepare functionalized TACs. $\eta^5$-cyclopentadienyl ligands with linked $\sigma$-heteroatom components have special reactivities [51]. In some examples linked amido-cyclopentadienyl complexes of group 4 transitions metals show unique polymerization properties [52].

In other complexes the cyclopentadienyl group is linked by an alkoxy component [51, 53] (fig. 44). More directly connected to this work are the analogous cyclopentadienyl complexes of chromium(III). The complex in fig. 45a shows only a low activity towards ethylene [54], whereas the complex fig. 45b gives activities of 8300 $gmmol^{-1}h^{-1}bar^{-1}$ [55, 56]. Additionally to the higher activity, the link can be used to direct the reactivity of such complexes in polymerization reactions in a wide range. Since polymerization experiments with $R_3$TACC$rCl_3$ complexes showed some very interesting properties [57], it was obvious to make similar functionalized triazacyclohexanes in order to prepare constrained geometry complexes of triazacyclohexanes analogous to fig. 45b.

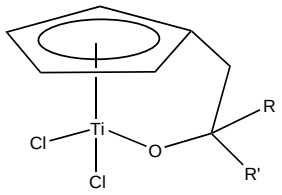



Figure 44: linked CpTi complex

But this is not the only reason, functionalized unsymmetrically substituted triazacyclohexanes are highly interesting. In [58] the activation of

dioxygen by a copper(I) complex of 1-pyridylmethyl-4,7-diisoproyl-1,4,7- triazanonane and consecutive mechanistic studies are reported. Such reactions are of possible relevance in biological and catalytic hydrocarbon oxidations mediated by copper active sites. Another possible use for $R'XR_2TAC$ is the preparation and characterization of heterobimetallic systems. Heterobimetallic systems like in fig. 46 [59] offer prospects for advantageous synergistic effects; for example, catalysis of olefin hydroformylation is markedly enhanced when a separate cobalt complex is added to a bis(phosphine)palladium catalyst [60].

### 2.3.5 Preparation of $(R'OH)R_2TAC$

$(R'CN)R_2TAC$ and $(R'OH)R_2TAC$ can be prepared using the same methods described in 2.3.3.

$$H_2N\text{-}(CH_2)_x\text{-}CN + 2\ R'NH_2 + 3\ CH_2O \longrightarrow (RCN)R'_2TAC$$
$$H_2N\text{-}(CH_2)_x\text{-}OH + 2\ R'NH_2 + 3\ CH_2O \longrightarrow (ROH)R'_2TAC$$


**a** **b**

Figure 45: A normal Cp*Cr(III) complex and a linked Cp*Cr(III) complex by Jolly

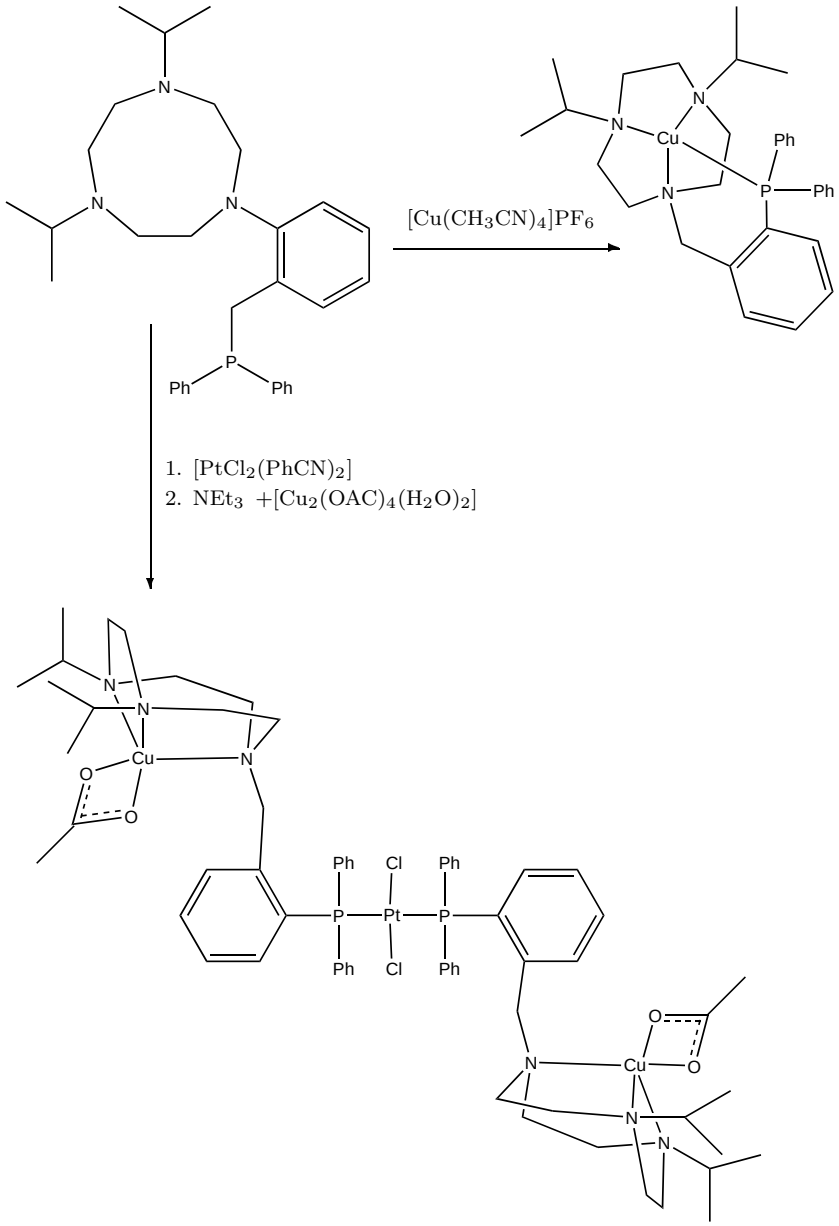



Figure 46: Examples of complexes of a donor functionalized unsymmetrical triazacyclononane [59]

(R′CN)$R_2$TAC shows no sign of rearrangements below 80 °C. They can, after drying with sodium, easily be purified by distillation or column chromatography. The (ROH)$R'_2$TAC, however, are much more prone for rearrangements. Figure 47 shows a literature known rearrangement of the related symmetrical compound $(ROH)_3$TAC [2]. In case of the unsymmetrically substituted (ROH)$R'_2$ a probably similar rearrangement slowly happens already at room temperature and is for obvious reasons irreversible. Regardless of their thermo lability, some of the smaller (ROH)$R'_2$TAC (R' = Me or Et) can be "pre-purified" by distillation when the heating time is kept short and the distillate is cooled at once with liquid nitrogen. In the distillate only TACs without or with only one -OH group can be found. $(R'OH)_2$RTAC and $(R'OH)_3$TAC remain in the residum. Purification by column chromatography is possible, too, but with both methods it was only possible to remove the byproducts with two or three -OH substituents. In the distillate, as well as in all fractions of column chromatography, the (ROH)$R'_2$TAC was always contaminated by 5-6% of $R'_3$TAC. The found percentage of $R'_3$TAC in all fractions, may be a sign for constant rearrangements on the column material. This rearrangement happened regardless of the column material used (silica gel and neutral aluminum oxide) and despite of a strong basic eluens

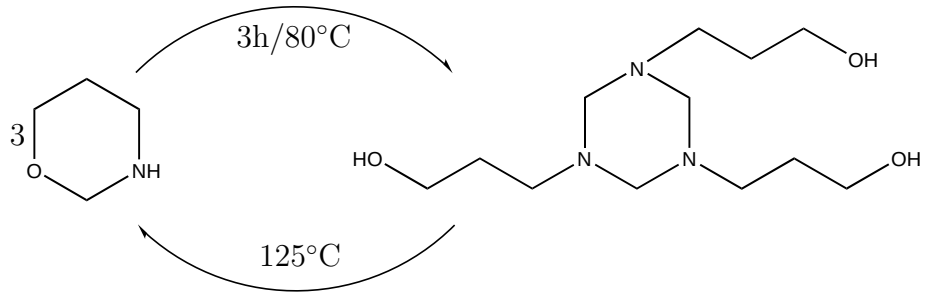



Figure 47: Equlibrium between $(PrOH)_3$TAC and tetrahydro-1,3-oxazine

with up to 50% of triethylamine.

Therefore, alternative methods had to be developed to remove the remaining $R'_3TAC$. By reaction with sodium the $(ROH)R'_2TAC$ can be turned into the correspondent alcoxide. The alcoxide is much more stable than the alcohol and can be heated to more than 100 °C without rearrangements. An even better method to get pure $(ROH)R'_2TAC$ is to add $Me_2SiCl_2$ to the mixture. The resulting $(R_2TAC\text{-}(CH_2)_x\text{-}O)_2Si(Me)_2$ are also very insensitive against heat.

$$2\ R'_2TACROH + Cl_2Si(CH_3)_2 \longrightarrow R'_2TACROSi(CH_3)_2ORTACR'_2 + 2\ HCl$$

After removal of the byproducts in vacuum or by recrystallization the siloxane can be cleaved cleanly with water giving highly pure $(ROH)R'_2TAC$.

$$R'_2TACROSi(CH_3)_2ORTACR'_2 + 2\ H_2O \longrightarrow 2\ R'_2TACROH + H_2Si(CH_3)_2$$

The product should be used at once or stored refrigerated.

### 2.3.6 Attempts to Prepare $(RCl)R'_2TAC$ from $(ROH)R'_2TAC$

Several attempts to convert the $(ROH)R'TAC$ into the corresponding chlorides using $SOCl_2$ failed. Regardless of solvents and temperatures, the reaction always lead to a black oil with a very complex $^1$H-NMR spectrum with no signs for intact triazacyclohexane rings. Another, very mild method to convert alcohols into chlorides is described in [61]:

$$ROH + Ph_3P + CCl_4 \longrightarrow RCl + Ph_3PO + HCCl_3$$

The result, however, was the same undefined mixture found in the former attempts when $SOCl_2$ was used. All observed facts indicate that $RClR'_2TAC$ are, at least at temperatures above 0 °C, unstable and decompose quickly. This observation is conform to prior observations made in this group on symmetrical $(RCl_3)TAC$.

### 2.3.7 Preparation of $(RNH_2)R'_2TAC$

The preparation of unsymmetrically substituted triazacyclohexanes with one nitrile substituent is relatively easy when the needed aminonitrile is available. The nitrile group can be reduced to the amine by $NaBH_4$ in alkaline solution:

$$2\ (RCN)R'_2TAC + NaBH_4/Ni + 4\ H_2O \longrightarrow 2\ (RNH_2)R'_2TAC + NaB(OH)_4$$

The presence of Raney nickel prevents the formation of undesired secondary amines [62].

### 2.3.8 Preparation of Bridged Triazacyclohexanes $R_2TAC$-R'-$R_2TAC$

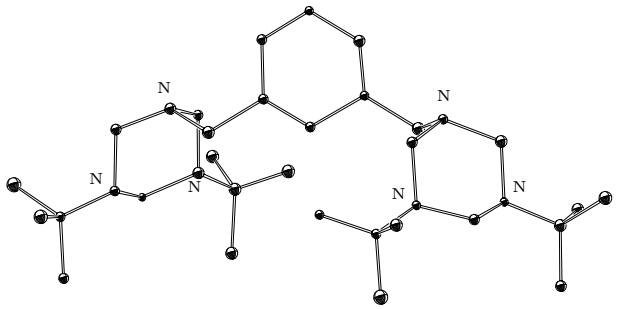



Figure 48: Two TAC rings connected by a m-xylylene bridge

For the preparation of bridged triazacyclohexanes (see fig. 48) the same methods as discussed earlier can be used. The bridged TACs are stable enough to remove volatile byproducts at $80 - 90\ ^\circ C$ in vacuo. So for the preparation of $R'_2TAC$-R-$R'_2TAC$ with R' = Me or Et the best method is to equilibrate a diamine $H_2N$-R-$NH_2$ at 130 °C with $Me_2TAC$ or $Et_3TAC$. Unfortunately, this method does not work for larger $R_3TAC$. Experiments with $^iPr_3TAC$ and $Bz_3TAC$ resulted in uncharacterized decomposition products. Nevertheless, bridged TACs with R = $^i$Pr, $^t$Bu can be obtained using

ethanol as solvent and a very low concentration of the amines. The isolation and purification of the product, however, is somewhat tedious. Regardless of the concentration and the ratio of the amines in ethanol, the formation of polymeric or oligomeric byproducts could not be prevented totally. Fortunately the more TACs are linked together, the less soluble they become in pentane, so they can be almost quantitatively removed when the desired product is extracted with cooled pentane. However, the huge excess of the symmetrical byproduct $R'_3$TAC has to be removed first, since it tends to carry the oligomers into the pentane solution. The remnants of multiply bridged TACs can be removed by dissolving the mixture in diethylether and filtering it through a short column of neutral aluminum oxide. Again it had been observed that surface effects of the column material catalyse the rearrangement of unsymmetrically substituted TACs. The filtrate usually contained a few percent of the symmetrically substituted TAC again, which now in the absence of multiple bridged TACs can be easily removed *in vacuo* or by recrystallization.

### 2.3.9 Attempts to Prepare Unsymmetrically Bridged Triazacyclohexanes ($\mathbf{R'_2}$TAC-R-$\mathbf{R''_2}$TAC)

The successful preparation of ($RNH_2$)$R'_2$TAC (see 2.3.7, p. 58) led to the question, whether unsymmetrically bridged TACs, i.e. different substituted TACs on each side of the bridge, can be prepared. Using the 'ethanol method' $Et_2(PrNH_2)$TAC was attempted to give with $MeNH_2$ $Et_2$TAC-$(CH_2)_3$-$Me_2$TAC, however, the only (bridged) product which could be isolated was the symmetrical $Me_2$TAC-$(CH_2)_3$-$Me_2$TAC.

### 2.3.10 Summary of $^{13}$C-NMR Data of Unsymmetrically Substituted $R_2R'TAC$

Table 3 shows the $^{13}$C-NMR signals of the ring carbon atoms of some selected unsymmetrically substituted $R_2R'TAC$. A comparison of the shifts of the symmetrically substituted $R_3TAC$ and $R'_3TAC$ with the shifts of the corresponding unsymmetrically substituted $R_2R'TAC$ shows, that for the position of the ring signals mainly the two direct R-N/R'-N neighbors are responsible. The influence of the third R-N substituent in the opposite location of the ring can be neglected at first approximation. The fourth column of table 3 shows the arithmetic average of the signal positions of the corresponding symmetrically substituted $R_3TAC$, i.e. $Bz_3TAC$ and $Me_3TAC$ for $Me_2BzTAC$. Not in all cases the $^{13}$C-NMR data for the $R_3TAC$ was available. In those cases $R_3TAC$ with similar substituents have been used ($^*Bz_3TAC$, $^{**}Et_3TAC$, $^{***}Pr_3TAC$). The positions of the other $^{13}$C ring signal lies, as expected, close to the position of the symmetrically substituted TAC. There might be a tendency to a slightly lower field shift of about 0.5 - 1.2 ppm.

The importance of the above results lies in the possibility to easily distinguish between an unsymmetrically substituted TAC and a mixture of the two corresponding symmetrically substituted $R_3TAC$ by $^{13}$C-NMR spectroscopy.

| $R_2R'TAC$ | $RCH_2R'$ | $(R_3TAC + R'_3TAC)/2$ | $RCH_2R$ |
|---|---|---|---|
| $(({}^tBu_2TAC)CH_2)_2Ph$ | 68.53 | 68.43* | 64.27 |
| $(({}^iPr_2TAC)CH_2)_2Ph$ | 71.15 | 71.29* | 68.34 |
| $((Et_2TAC)CH_2)_2Ph$ | 73.88 | 73.85* | 73.37 |
| $((Me_2TAC)CH_2)_2Ph$ | 74.55 | 75.43* | 76.86 |
| $(Et_2(EtO)TAC)_2SiMe_2$ | 74.41 | - | 74.20 |
| $(Me_2(EtO)TAC)_2SiMe_2$ | 75.42 | 75.45** | 78.41 |
| $Et_2(PrNH_2)TAC$ | 74.00 | 73.78*** | 73.63 |
| $Me_2(PrNH_2)TAC$ | 75.09 | 75.368*** | 78.09 |
| $Me_2(PrOH)TAC$ | 74.92 | 75.368 | 77.41 |
| ${}^iPr_2(EtOH)TAC$ | 69.51 | 71.41** | 68.89 |
| $Et_2(EtOSiMe_3)TAC$ | 74.12 | - | 74.34 |
| $Et_2(EtCN)TAC$ | 73.07 | - | 74.48 |
| $Et_2(EtOH)TAC$ | 72.87 | - | 75.36 |
| $Me_2(EtCN)TAC$ | 74.30 | 75.54* | 78.75 |
| $Me_2(EtOH)TAC$ | 73.71 | 75.54* | 79.55 |
| $Me_2OctTAC$ | 75.15 | 75.86 | 78.28 |
| $Me_2BzTAC$ | 74.66 | 75.43 | 78.31 |

Table 3: $^{13}$C-NMR signals of the ring carbon atoms of unsymmetrically substituted TAC. Values used to calculate averages [ppm]: $Me_3TAC$ 77.12, $nPr_3TAC$ 74.23, $(PrOH)_3TAC$ 73.6, $iPr_3TAC$ 68.85, $Oct_3TAC$ 74.6, $Et_3TAC$ 73.97, $Bz_2TAC$ 73.73; Substitutes for missing $R_3TAC$ data: $^*Bz_3TAC$, $^{**}Et_3TAC$, $^{***}Pr_3TAC$

# 3 Some Possible Prospects for Future Research Based on the Results in this Work

This chapter subsumes borderline cases of this work which either do not fit in one of the previous chapters or which were only superficially dealt with in some overview experiments with no hard enough data for a proper discussion, but are nevertheless interesting enough for further research.

## 3.1 13-alkyl-1,5,9-triazatricyclo[7.3.1.$0^{5,13}$]-tridecanes

Compared with the good results of triazacyclohexanes in polymerization reactions, there appears to be no obvious advantage in using RTATC as ligand. The ligand is more difficult and more expensive to prepare and the catalytic activity of its chromium complexes is notably lower then those of comparable triazacyclohexane complexes.

However, the triazacyclohexane chromium complexes examined in this group do not solely catalyse the polymerization of ethylene, but show interesting and unexpected abilities in selectively trimerizing $\alpha$-olefins. So before RTATC complexes are disregarded as catalysts in favor for the $R_3$TAC complexes, at least some overview experiments should be made, in case these complexes have other unexpected properties like the formation of unusual molecular weight distributions.

An interesting "byproduct" of the work on RTATC complexes is the chromium anion in fig. 49. An attempt to alkylate HTATCCr$Cl_3$ with $(CH_3)_3CH_2Li$ according to:

$$\text{HTATCCrCl}_3 + 3\ (\text{CH}_3)\text{CH}_2\text{Li} \longrightarrow \text{HTATCr}(\text{CH}_2(\text{CH}_3))_3 + 3\ \text{LiCl}$$

The result was a deep purple liquid, at room temperature extremely air

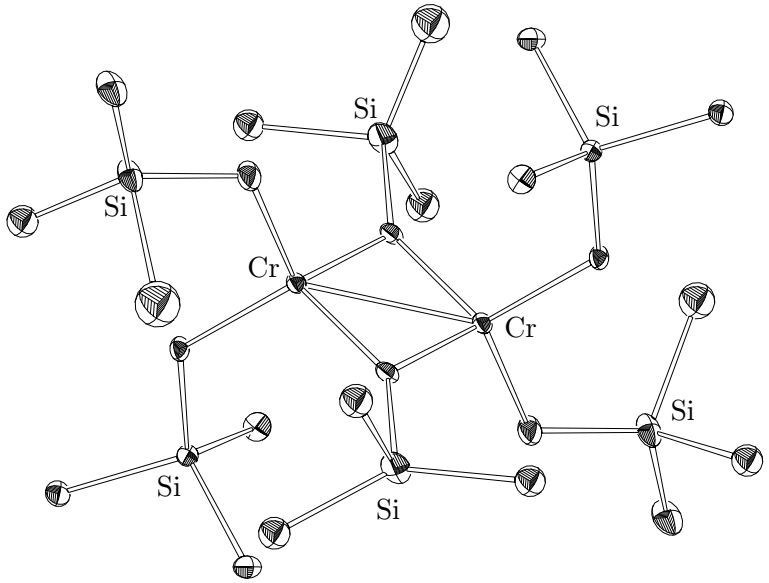



Figure 49: Result of an alkylating attempt of $HTATCCrCl_3$ with $(CH_3)_3CH_2Li$

and water sensitive chromium complex, which can be distilled in high vacuum. However, according to the obtained x-ray crystal structure the complex actually is an alkyl chromium complex, but does not contain coordinated HTATC. Instead it contains two uncoordinated HTATC and one $[TATC]^+$ cation. The chromium compound therefore must be mono anionic. The complex is bi-nuclear with two alkyl bridges and two terminal $CH_2Si(CH_3)_3$ and an inversion center between the two Cr-atoms. The terminal $CH_2Si(CH_3)_3$ units have Cr-C distances of $203 - 204$ pm and Cr-C-Si angles of $123 - 126$ °, which can be expected to be a regular Cr-C singular bond, and therefore can doubtless be formulated as $[CH_2Si(CH_3)_3]^-$. The bridging "$CH_xSi(CH_3)_3$" units have unusual Cr-C bond lengths (185 pm) and Cr-C-Cr resp. Cr-C-Si bond angles (89 ° and $131 - 139$ °). The $Cr_2C_2$ unit is roughly square planar, the Cr-C bonds are clearly stronger than singular bonds. There are many

publications with similar alkyl or amido bridged chromium complexes with a wide range of oxidation states [63, 64, 65, 66, 67]. Characteristic values for Cr-C/N bonds and Cr-C/N-Cr angles are:

- $Cr^{II}(\mu - R^{-})Cr^{II}$: 218 pm, 62 ° (not planar)
- $Cr^{III}(\mu - R^{-})Cr^{III}$: 219 pm, 73 ° (planar)

The bridging units have considerably longer bonds and smaller angles, so alkylidene or alkylidine bridges rather than alkyl bridges should be considered.

- $Cr^{III}(\mu - CH_2^{2-})Cr^{III}$: 204 pm, 72 ° (triple bridged)
- $Cr^{IV}(\mu - NR^{2-})Cr^{IV}$: 182 pm, 88 ° (planar)
- $Cr^{V}(\mu - NR^{2-})Cr^{V}$: 182 pm, 87 ° (planar)

The bond lengths and angles in this anion are similar to those in the imido bridged $Cr^{IV}$ or $Cr^{V}$ dimers. This would be consistent with the following formula:

$$[(Me_3SiCH_2)_2Cr^{IV,V}(\mu - CSiMe_3)_2Cr^{IV,V}(CH_2SiMe_3)_2]^{(0-2)-}$$

Actually, there is a similar $[Nb_2^{V}(\mu - CSiMe_3)_2(CH_2SiMe_3)_4]$ complex which was formed by an alkylation of $NbCl_5$ with $Me_3SiCH_2MgCl$ [68]. Due to the slightly larger ionic radius of niobium the bond lengths are about 12 pm longer. The $Nb_2C_2$ unit is just like the $Cr_2C_2$ unit square planar. Because of the neutrality of charge the chromium complex has to carry a negative charge. Therefore the complex is formulated as:

$$(TATC^{+})[Cr^{IV}Cr^{V}(\mu - CSiMe_3)_2(CH_2SiMe_3)_4]^{-} \cdot (HTATC)_2 \ \mathbf{14}$$

The oxidative Alkylation of $Cr^{III}Cl_3$ with LiR (R among others $CH_2SiMe_3$) often resulted in volatile, purple $Cr^{IV}R_4$ compounds [69]. The formation of Schrock carbenes and carbines by $\alpha$-H elimination and cleavage of $SiMe_4$ from high valent alkyl complexes is well known, too. Probably analogous to the niobium compound, the $Cr^V$ compound $Cr_2(CSiMe_3)_2(CH_2SiMe_3)_4$ was formed which was distilled along with the HTATC. Finally, the chromium has been partially reduced by the HTATC giving **14**.

The comparison of **14** with known similar structures surely allows to draw the conclusions above. Nevertheless, a backup by experimental data is to be favored. One, yet unrealized, but for future work still interesting idea was to decompose the compound with $D_2O$ and analyze the forming fragments by mass spectroscopy. This way it should be easy to decide what kind of $Me_3SiCH_2$ bridges there really are.

## 3.2 Copper Complexes of Triazacyclohexanes

Though the most interesting discovery during the work on $R_3$TAC copper complexes was made, and though the reaction which formed the crystals which contain the unusual $[Cu_2Cl_4]^{2-}$ anion is not fully understood yet (see section 2.2.1, p. 40), these structures are reproducible. Therefore this system should be accessible for a theoretical evaluation which could help resolve the controversity concerning the existence of *cuprophilicity*.

Other prospects for the work on $R_3$TAC copper complexes can be found in the work by Tolman and coworkers [70, 71, 72, 18, 58]. The studies on copper complexes of triazacyclononanes in these publications have all a very interesting bioinorganic aspect like catalytic oxygen activation or denitrification. Only a very small part of these experiments have yet been repeated using triazacyclohexanes (see section 2.2.2, 42). The foundation for further

comparisons of copper complexes analogous to the triazacyclononane complexes has been prepared by the development of unsymmetrically substituted triazacyclohexanes.

## 3.3 Unsymmetrically Substituted Triazacyclohexanes

This leads to the question of future studies on unsymmetrically substituted triazacyclohexanes. Though the methods developed in this work allow a broad variation of unsymmetrical $R'R_2TAC$, there will always be substituents which cannot be introduced by these methods (e.g. section 2.3.6, p. 57). So there is still room for further studies on $R'R_2TAC$.

Actually, no serious attempts to make complexes with these ligands had been done, yet. Some "quick and dirty" overview experiments have been made and may outline the path for future research, but for a more thorough discussion the available analytical data is insufficient. Therefore the following equations are best to be viewed as an advanced guess or a working hypothesis for further experiments.

Chromium complexes with the usual triazacyclohexanes are purple solids which are relatively inert against air and water. Reactions of $(THF)_3CrCl_3$ with triazacyclohexanes with one OH-group gave light green solids which easily react with water. The resulting dark green products are highly soluble in water and other polar solvents, there are no hints that the ligand is cleaved. The following reaction might explain this observation:

$$R_2R'OTACCrCl_2 + 2\ H_2O \longrightarrow [R_2R'OTACCr(OH_2)_2]Cl_2$$

When $R_2R'OTACCrCl_2$ is stirred in $SOCl_2$ or $ClSi(CH_3)_3$ the color of the solid changes to a shade of purple found in complexes with symmetrical TAC. This effect would be easily explained by the reaction in figure 50 with

$SOCl_2$. This way it should be possible to prepare unsymmetrical functional-

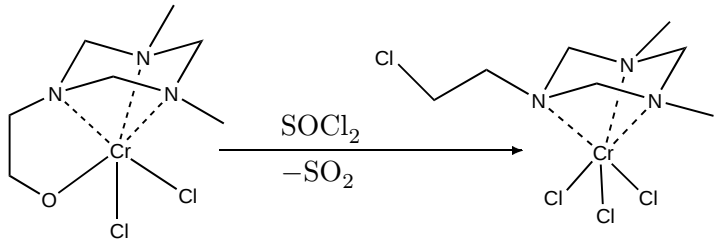



Figure 50: Probable reaction of linked alkoxyTAC complexes with $SOCl_2$

ized $R'R_2TAC$ which are not accessible by the methods described in section 2.3.

A surprisingly similar observation can be made using bridged triazacyclohexanes. The green products of the reaction of $(THF)_3CrCl_3$ with $R_2TAC\text{-}CH_2\text{-}m\text{-}C_6H_4\text{-}CH_2\text{-}TACR_2$ are air and water sensitive. An experiment with two TAC rings bridged by a hexyl group indicate that this effect is independent of the bridging unit. Another experiment with simple non-functionalized unsymmetrically substituted $R_2R'TAC$ shows also, that this is not an effect of the dissymmetry of the ligand. The complexes with the $R_2R'TAC$ described in section 2.3.3 were not notably different from complexes with symmetrical triazacyclohexanes. Figure 51 shows one attempt to explain the similarity of this complex class with the

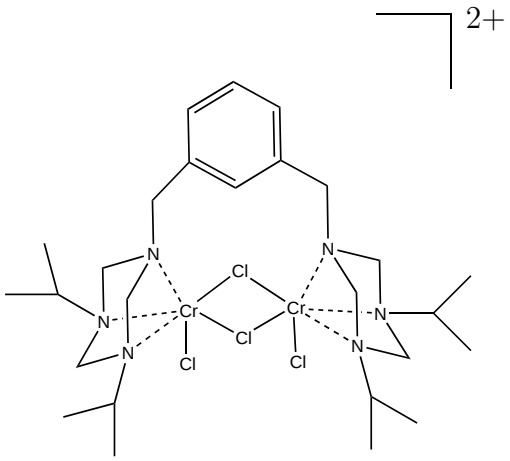



Figure 51: Possible chromium complexes with a bridged TAC-ligand?

hydroxy-TAC chromium complexes.

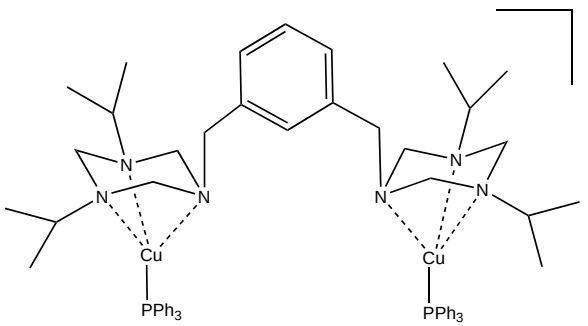



Figure 52: Probable structure of a Cu(I) complex with a bridged triazacyclohexane

The first attempt to make Cu(I) complexes with the m-xylylene bridged isopropyl TAC and $[Cu(CH_3CN)_4]BF_4$ analogous to the Cu(I) complexes in section 2.2.2, p. 42 gave a product with a very complex $^1$H-NMR spectrum, which could not be interpreted. However, the same product treated with $PPh_3$ afterwards gave the spectrum in fig. 53. Though this spectrum is still insufficient to gain reliable information, it does show

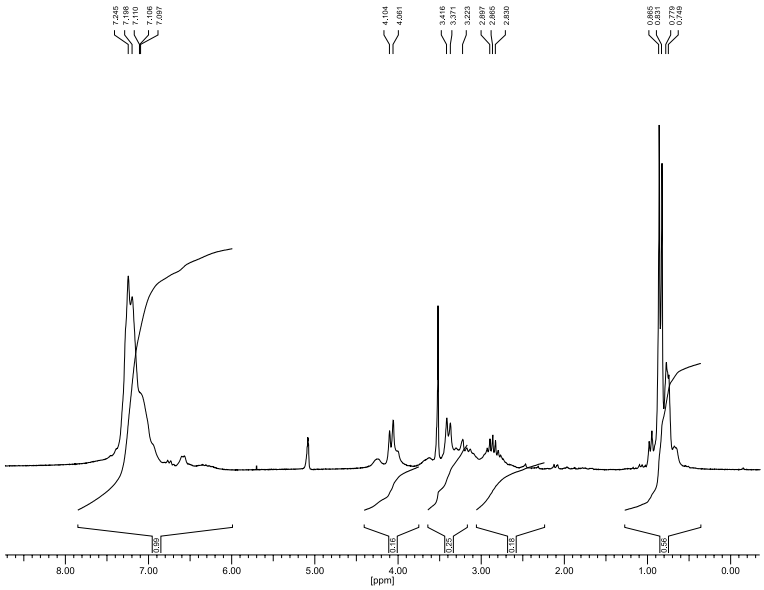



Figure 53: Insufficient $^1$H-NMR spectrum of $[PPh_3Cu(^iPr_2TAC)CH_2PhCH_2(^iPr_2TAC)CuPPh_3](BF_4)_2$

roughly the expected signals for the complex in fig. 53. Which are mainly the doublets for the endo- and exo-protons of the ring hydrogen atoms at 4.08 and 3.39 ppm.

# 4 Summary and Conclusions

The motivation for this thesis was to expand the main field in the group of Randolf D. Köhn, i.e. the use of triazacyclohexane complexes as polymerization catalysts. With this intention three different, though related, aspects have been explored.

- The preparation and characterization of compounds structurally analogous to the triazacyclohexanes, namely the orthoamides (RTATC) and a selection of the chromium, iron, and copper and zinc complexes.
- The application of triazacyclohexanes in copper systems with bioinorganic interest.
- The preparation and characterization of new classes of unsymmetrically substituted triazacyclohexanes.

## 4.1 13-alkyl-1,5,9-triazatricyclo[7.3.1.$0^{5,13}$]-tridecanes

New and easier routes to a wide range of RTATC had been developed by alkylation of the $[TATC]^+$ cation with lithium, sodium or potassium alkyl reagents. On the basis of several Cr(III), Fe(III), Cu(II), and Zn(II) complexes it could be shown, that the chemistry of the RTATC ligands and their complexes is very similar to the chemistry of the $R_3TAC$ systems. However, the preparation of the RTATC ligands is much more complicated and expensive than that of the $R_3TAC$ ligands . Moreover, a polymerization experiment with ethylene indicated that the activity of RTATC chromium complexes as catalyst is much lower than of similar $R_3TAC$ complexes. This is not surprising, since it is concurrent with the fact that RTATC chromium complexes are much less soluble than $R_3TAC$ chromium complexes and re-

sults gained by the BASF show that the activity of those complexes strongly correlates with their solubility.

## 4.2 Copper Complexes of Triazacyclohexanes

$[Cu(MeCN)_4]^+$ reacts readily with $R_3TAC$ (R = $^i$Pr, Bz, Cy) to cationic Cu(I) complexes $[(R_3TAC)Cu(MeCN)]^+$. The rather air sensitive $[(R_3TAC)Cu(MeCN)]^+$ complexes can be stabilized by replacing the MeCN ligand with $PPh_3$ or THF. Due to their diamagnetism and the ease the $[(R_3TAC)Cu(PPh_3)]BF_4$ form suitable crystals for x-ray crystal structure analysis, Cu(I) complexes belong to the best characterized $R_3TAC$ complexes today.

A real surprise, however, was the chemistry of a Cu(II) complex with $Me_3TAC$. The "$Me_3TACCuCl_2$" complex can coordinate another $Me_3TAC$, resulting in an unusual coordination geometry which allows slow reduction of the Cu(II) to Cu(I) by $Me_3TAC$. The formed Cu(I) ion $[Cu_2Cl_4]^{2-}$ shows the first cuprophilic Cu-Cu interaction between two anions which must therefore be stronger than the electrostatic repulsion.

## 4.3 Unsymmetrically Substituted Triazacyclohexanes

Synthesis of triazacyclohexanes with a mixture of two amines in a suitable solvent such as ethanol or exploitation of the equilibria between $R_3TAC$ and $R'NH_2$ above 100 °C yields mixtures of unsymmetrically substituted $R_2R'TAC$ which could be separated by various methods below 100 °C The pure and dry unsymmetrically substituted $R_2R'TAC$ are stable at room temperature and even at higher temperatures for short periods and can best be identified by their very characteristic $^{13}C$ NMR signals for the ring carbon atoms.

This way three different types of unsymmetrically substituted $R_2R'TAC$ (simple $R_2R'TAC$, see 2.3.1, p. 49; functionalized $R_2(RX)TAC$, see 2.3.4m p. 52; bridged $R_2TAC$-R'-$R_2TAC$, see 2.3.8, p. 58) had been prepared and their basic properties had been studied on at least three examples.

# 5 Experimental Section

## 5.1 General Considerations

All syntheses, except were noted, were carried out under an atmosphere of deoxigenated and dried argon (passed through an activated column of molecular sieve and a column of BASF catalyst) using standard Schlenk, high vacuum line or glove box techniques. Moisture sensitive compounds were stored in a glove box (Braun). Hexane, pentane, diethylether, THF were dried and stored over sodium/benzophenone, $CH_2Cl_2$, 1,2-dichloroethane, acetone, acetonitrile and nitromethane were dried and stored over $CaH_2$. Usually the solvents were directly vacuum transferred into the reaction flasks.

NMR spectra were obtained on either a Bruker ARX 200 (200 MHz) or on a Bruker ARX 400 (400 MHz) spectrometer.

Elemental analyses were obtained on a Perkin-Elmer Series II CHNS/O Analyzer 2000 or using the analytical service of the Humboldt-University in Berlin.

Mass spectra were obtained on a Varian MAT 331 A by electron impact ionization at 70 eV.

Atomic absorption spectroscopy was performed on a Perkin-Elmer 2380 Atomic Absorption Spectrometer.

IR spectra were obtained on a Perkin Elmer 580 B infrared spectrometer, UV/VIS spectra were recorded on a Beckman DU 650 spectrophotometer.

## 5.2 Ligands

### 5.2.1 13-Alkyl-1,5,9-triazatricyclo[7.3.1.$0^{5,13}$]-tridecanes

1,5,9-Triazatridecylium bromide: $\mathbf{3}^+Br^-$

1,5,7-triazabicyclo[4.4.0]dec-5-ene **15** (15.0 g, $M = 139.2$ gmol $^{-1}$, 108 mmol) was dissolved in THF (250 ml) and NaH (2.6 g, $M$= 24.0 gmol$^{-1}$, 108 mmol) was added. 1,3-Dibromoprompane (21.75 g, $M = 201.9$ gmol$^{-1}$, 108 mmol), dissolved in 25 ml of THF, was added dropwise at $-78$ °C. After slow warming to ambient temperature and stirring for 24 h, the solution was decanted from the solids which were washed with $Et_2O$ (100 ml). Extraction with 150 ml of $CH_2Cl_2$ in several portions and removal of the solvent yielded 19 g of impure $\mathbf{3}^+Br^-$. To purify the bromide it was solved in about 200 ml of $CH_2Cl_2$. The bromide is precipitated again by pouring the solution into $200 - 400$ ml of diethylether. This procedure was repeated up to fifty times until the precipitate was pure white and the solution was colorless. Yield: 5 g (18%) of pure white $\mathbf{3}^+Br^-$ ($M = 260.2$ gmol$^{-1}$), m.p. 72 °C.

| $C_{10}H_{18}N_3Br$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 45.51 | 6.99 | 16.15 |
| Calc: | 46.16 | 6.97 | 16.15 |

**Infrared Spectrum** (KBr; $\nu$/cm$^{-1}$)

3940m, 3554s, 3464s, 3402s, 2942s, 2922s, 2866s, 2806m, 2702m, 2363w, 2214w, 2064w, 1816w, 1740w, 1590s, 1490w, 1457w, 1429w, 1380s, 1343w, 1327s, 1307w, 1285m, 1245m, 1232m, 1189w, 1136w, 1111w, 1069m, 1040m, 981w, 908w, 890w, 840w, 689m, 612w, 529w, 500w, 460m, 446m

1,5,9-Triazatridecylium Tetrafluoroborate: $\mathbf{3}^+BF_4^-$

$\mathbf{3}^+BF_4^-$ was prepared according to [21].

1,5,9-Triazatridecylium Tetraphenylborate: $\mathbf{3}^+BPh_4^-$

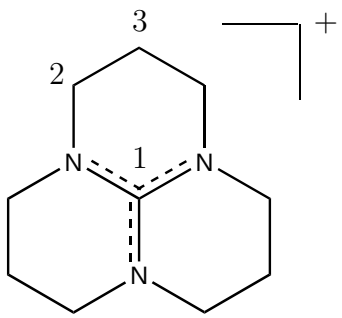
19 g of impure $\mathbf{3}^+Br^-$ ($M = 260.2\ gmol^{-1}$) was dissolved in 150 ml of water. Addition of an aqueous solution of 25 g ($M = 342.2\ gmol^{-1}$, 73 mmol) of $NaBPh_4$ precipitated $\mathbf{3}^+BPh_4^-$ which was dried *in vacuo* and Soxhlet-extracted with acetone. 20 g (37% relative to **15**) of colorless $\mathbf{3}^+BPh_4^-$ ($M = 499.5\ gmol^{-1}$) was obtained, m.p. 269 °C.

| $C_{34}H_{38}N_3B$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 81.25 | 7.75 | 8.44 |
| Calc: | 81.75 | 7.67 | 8.41 |

**Infrared Spectrum** (KBr; $\nu/cm^{-1}$)

3051s, 3039s, 3026s, 3001s, 2996s, 2982s, 2969s, 2939s, 2877s, 1942w, 1884w, 1809w, 1606s, 1598s, 1581m, 1477m, 1471m, 1455w, 1439w, 1427m, 1382m, 1377m, 1324m, 1305m, 1267w, 1243w, 1219w, 1151w, 1144w, 1068w, 1059w, 1031w, 848w, 842w, 743m, 735m, 708s, 693m, 626w, 614m, 605s, 479w, 462w

**$^1$H and $^{13}$C NMR Data**



| $^1$H-**NMR** (200 MHz, $CDCl_3$) | | | $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$) |
|---|---|---|---|
| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | $\delta$(ppm) |
| 1 | | | 149.56 |
| 2 | 3.29 | 12t | 47.54 |
| 3 | 2.00 | 6tt | 20.16 |
| B$Ph_4$ | 7.7-7.0 | 20m | 145.6, 130.4, 127.0, 126.6 |

1,5,9-Triazatricyclo[7.3.1.$0^{5,13}$]-tridecane : **16**

HTATC was prepared according to literature methods [21].

| $C_{10}H_{19}N_3$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 65.22 | 11.01 | 23.28 |
| Calc: | 66.26 | 10.56 | 23.18 |

**Infrared Spectrum** ($CCl_4$; $\nu$/cm$^{-1}$)

2939s, 2919s, 2840w, 2800m, 2795m, 2740, 2700w, 2670m, 2600w, 2580w, 2495w, 2450w, 2430w, 2400w

**$^{13}$C-NMR Data** (50 MHz; $CDCl_3$)

99.8, 53.4, 23.5

13-Methyl-1,5,9-triazatricyclo[7.3.1.$0^{5,13}$]-tridecane : **17**

5 g of $TATCBF_4$ ($M$ = 267.1 gmol$^{-1}$, 18.72 mmol) were mixed with 0.42 g of MeLi ($M$ = 22.0 gmol$^{-1}$, 19.11 mmol). 50 ml of THF were added via vacuum transfer. After stirring for 12 h the solid was filtered off and the solvent removed in vacuum. Yield: 2.1 g (57%) of **17** ($M$ = 195.3 gmol$^{-1}$) as colorless, oily liquid.

**Infrared Spectrum** ($CCl_4$; $\nu$/cm$^{-1}$)

2942s, 2920s, 2885m, 2835m, 2800s, 2780m, 2740s, 2695w, 2658w

**$^{13}$C -NMR Data** (50 MHz; DMSO-$d_6$)

85.3, 48.1, 23.1, -0.8

13-Butyl-1,5,9-triazatricyclo[7.3.1.$0^{5,13}$]-tridecane : **18**

2.0 g ($M$ = 260.2 gmol$^{-1}$, 7.7 mmol) of thoroughly dried pure **3**$^{+}$Br$^{-}$ were dissolved in 25 ml of THF. Under rapid stirring and water cooling 4 ml of butyl-lithium (2.0 M, 8 mmol) in cyclohexane were added. After 1 h stirring at roomtemperature the solid was filtered off and the solvent removed in vacuum. Yield: 1.5 g (83%) of pure **18** ($M$ = 237.4 gmol$^{-1}$) as colorless, oily liquid.

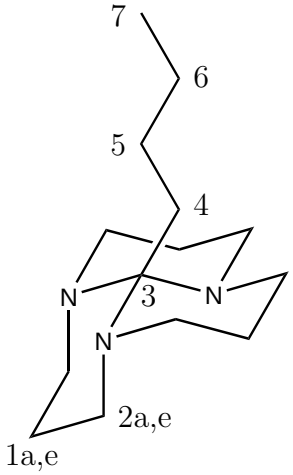
**Infrared Spectrum** (KBr/film; $\nu$/cm$^{-1}$)

2946s, 2885s, 2854s, 2819s, 2804s, 2758m, 2745m, 2697m, 2676m, 1467m, 1459s, 1445m, 1431m, 1382m, 1352m, 1344s, 1320s, 1294m, 1273m, 1250m, 1226m, 1216m, 1199m, 1184s, 1175s, 1124m, 1110s, 1093s, 1075m, 1019m, 988m, 957s, 947m, 905s, 880m, 833m, 824m, 609w, 572w, 524w, 513w, 494w, 482w, 443w, 439w, 435w, 428w, 423w, 420w, 416w, 413w

**Mass Spectrum** (70 eV; 43 °C)

| m/z | $I_{relative}$% | fragment | m/z | $I_{relative}$% | fragment |
|---|---|---|---|---|---|
| 236 | (8) | [**18**]$^{+}$ | 180 | (100) | [**3**]$^{+}$ |

**$^{1}$H and $^{13}$C NMR Data**



| $^1$H-**NMR** (200 MHz, $CDCl_3$) | | | | $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$) |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
| 3 | | | | 86.43 |
| 1a,e | 2.79 | - | 12m | 48.35 |
| 2a,4 | 1.93 | - | 5m | 21.33, 19.85 |
| 2e,5,6 | 1.28 | - | 7m | 21.33, 25.20, 23.35 |
| 7 | 0.89 | 7 | 3t | 14.27 |

13-Trimethyl-silyl-methyl-1,5,9-triazatricyclo[7.3.1.$0^{5,13}$]-tridecane : **19**

To a mixture of 2.1 g (8.1 mmol) carefully dried pure $\mathbf{3}^+Br^-$ ($M$ = 260.2 gmol$^{-1}$) and 0.76 g of $(CH_3)_3SiCH_2Li$ ($M$ = 79.1 gmol$^{-1}$, 8.1 mmol) 25 ml of THF were added under rapid stirring and water cooling. After stirring at room temperature for 1 h the solid was filtered off and the solvent removed in vacuo. Yield: 1.97 g (91%) of pure white **19** ($M$ = 267.5 gmol$^{-1}$), m.p. 68 °C

| $C_{14}H_{29}N_3Si$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 62.68 | 10.82 | 15.83 |
| Calc: | 62.86 | 10.93 | 15.71 |

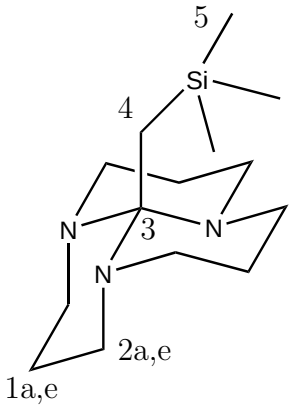
**Infrared Spectrum** (KBr; $\nu$/cm$^{-1}$)

2945s, 2927s, 2893m, 2837m, 2809m, 2756m, 2693w, 2674w, 1476w, 1466m, 1457m, 1443m, 1433m, 1414w, 1394m, 1380m, 1350s, 1343s, 1319s, 1291m, 1272s, 1241m, 1224m, 1195s, 1172m, 1145m, 1129m, 1122m, 1110s, 1103s, 1094s, 1077s, 1063m, 1020w, 955s, 945m, 905m, 888s, 862s, 851s, 821s, 791w, 770m, 759m, 727w, 684m, 640w, 617w, 600w, 569w, 469w, 423w

**Mass Spectrum** (70 eV; 49 °C)

| m/z | $I_{relative}$% | fragment | m/z | $I_{relative}$% | fragment |
|---|---|---|---|---|---|
| 267 | (8) | $[\mathbf{19}]^+$ | 225 | (9) | $[\mathbf{3} - CH_2SiH_3]^+$ |
| 252 | (17) | $[\mathbf{3} - CH_2Si(CH_3)_2]^+$ | 180 | (100) | $[\mathbf{3}]^+$ |
| 239 | (8) | $[\mathbf{3} - CH_2SiH_2CH_3]^+$ | | | |

**$^1$H and $^{13}$C NMR Data**




$^1$H-**NMR** (200 MHz, $CDCl_3$) $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$)

| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
|---|---|---|---|---|
| 3 | | | | 87.19 |
| 1a,e | 2.73 | - | 12m | 48.80 |
| 2a | 1.92 | - | 3m | 21.60 |
| 4 | 1.47 | - | 2s | 10.54 |
| 2e | 1.30 | - | 3m | 21.60 |
| 5 | 0.00 | - | 9s | 0.36 |

13-Phenyl-1,5,9-triazatricyclo[7.3.1.$0^{5,13}$]-tridecane : **20**

$\mathbf{3}^+BPh_4^-$ ($M$ = 499.5 gmol$^{-1}$, 4.0 g, 8.0 mmol) and phenyl sodium ($M$ = 100.1 gmol$^{-1}$, 1.6 g, 16.0 mmol) were refluxed in hexane for three days. The suspension became light brown during that time. The solids were filtered

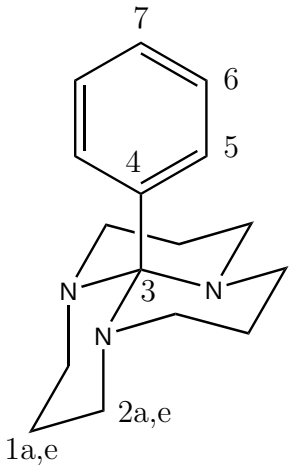
off and extracted with hexane. The solvent of the combined hexane extracts was removed *in vacuo*. The remaining waxy solid was redissolved in ether and filtered through neutral alumina. The solvent was removed *in vacuo* and the remaining crude **20** sublimed at 90 °C/1.3 Pa. 0.97 g (48%) of colorless crystalline **20** ($M = 257.3$ gmol$^{-1}$) were obtained, m.p. $97 - 98$ °C.

| $C_{16}H_{23}N_3$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 74.64 | 9.58 | 15.94 |
| Calc: | 74.67 | 9.01 | 16.33 |

**Infrared Spectrum** (KBr; $\nu$/cm$^{-1}$)

3454m, 3112w, 3092w, 3057w, 3050w, 3029w, 3015w, 2997w, 1693w, 1669w, 1648w, 1628w, 1597w, 2935s, 2922s, 2895m, 2885m, 2865m, 2836s, 2813m, 2785m, 2776m, 2734m, 2721m, 2700m, 2668m, 2566w, 2008w, 1972w, 1953w, 1935w, 1905w, 1881w, 1841w, 1820w, 1808w, 1765w, 1736w, 1581w, 1552w, 1488s, 1476s, 1465m, 1454s, 1443s, 1430m, 1399w, 1383w, 1376m, 1358s, 1343s, 1323s, 1314m, 1308m, 1294m, 1277s, 1267s, 1238m, 1223m, 1221m, 1215m, 1197s, 1181s, 1152s, 1125m, 1111s, 1103s, 1067s, 1051m, 1031m, 999s, 975w, 969w, 950s, 931s, 922m, 915m, 904m, 890m, 882m, 840w, 829w, 825w, 813w, 752s, 707m, 701s, 667m, 621m, 609m, 583m, 548m, 525m, 494w, 466w, 434w, 421m

**$^1$H and $^{13}$C NMR Data**




| $^1$H-**NMR** (200 MHz, $CDCl_3$) | | | | $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$) |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
| 3 | | | | 86.9 |
| 5-8 | 7.8-7.2 | | 5m | 145.6, 130.4 |
| | | | | 127.0, 126.6 |
| 1a,e | 2.96 | - | 12m | 48.1 |
| 2a | 2.11 | - | 3m | 20.9 |
| 2e | 1.48 | - | 3m | 20.9 |

13-Benzyl-1,5,9-triazatricyclo[7.3.1.$0^{5,13}$]-tridecane : **21**

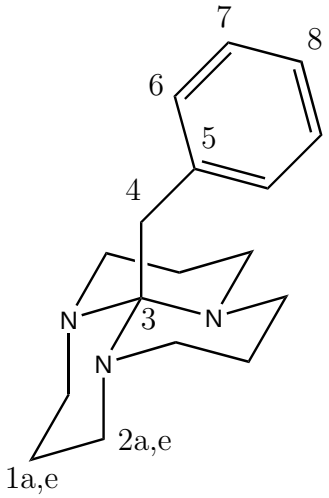
**3**$^+BPh_4^-$ ($M$ = 499.5 gmol$^{-1}$, 10.0 g, 20.0 mmol) and benzyl sodium ($M$ = 114.1 gmol$^{-1}$, 3.1 g, 19.9 mmol) were refluxed in toluene for three days. The suspension became light brown during that time. Work-up analogous to **20** and sublimation at 100 °C/1.3 Pa yielded 2.51 g (46%) of colorless crystalline **21** ($M$ = 271.4 gmol$^{-1}$), m.p. 117 − 119 °C

| $C_{17}H_{35}N_3$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 75.03 | 9.66 | 15.34 |
| Calc: | 75.23 | 9.28 | 15.48 |

**Infrared Spectrum** (KBr; $\nu/\mathrm{cm}^{-1}$)

3475w, 3082m, 3065m, 3017m, 2996m, 2948s, 2886s, 2839s, 2823s, 2793s, 2752s, 2731m, 2669w, 1946w, 1806w, 1605w, 1598w, 1493s, 1480w, 1467e, 1457w, 1443w, 1432w, 1394w, 1382m, 1351s, 1329w, 1319s, 1308w, 1293w, 1285w, 1269s, 1231w, 1212w, 1189s, 1172w, 1161s, 1135w, 1120w, 1108s, 1082m, 1047w, 1033w, 1002w, 961s, 946w, 924w, 907m, 901m, 888m, 874w, 865w, 842w, 833w, 812w, 803w, 787m, 735s, 698s, 670w, 623w, 606w, 600m, 568w, 523w, 473w, 421w

**$^1$H and $^{13}$C NMR Data**



| $^1$H-**NMR** (200 MHz, $CDCl_3$) | | | | $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$) |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
| 3 | | | | 86.8 |
| 5-8 | 7.6-7.3 | | 5m | 145.6, 130.4 |
| | | | | 127.0, 126.6 |
| 4 | 3.43 | | 2s | 25.84 |
| 1a,e | 2.96 | - | 12m | 48.6 |
| 2a | 2.13 | - | 3m | 21.4 |
| 2e | 1.50 | - | 3m | 21.4 |

13-[4-tert-Butyl-benzyl]-1,5,9-triazatricyclo[7.3.1.$0^{5,13}$]-tridecane : **22**

**3**$^+BPh_4^-$ ($M$ = 499.5 gmol$^{-1}$, 5.79 g, 11.6 mmol) and 4-$^t$Bu-benzyl potassium ($M$ = 186.3 gmol$^{-1}$, 2.55 g, 13.68 mmol) were heated for 24 h in about 30 ml of 4-$^t$Bu-toluene at 135 °C. During this time the red suspension turns slowly to light brown. The solid is filtered of and washed with 4-$^t$Bu-toluene. The washing solutions are combined with the filtrate and filtered through neutral alumina. Afterwards the solvent is removed at 120 °C under reduced pressure. The remaining light yellow solid is sublimed at 110 °C in vacuum (1.3 Pa). Yield: 0.87 g ($M$ = 327.5 gmol$^{-1}$, 2.66 mmol, 23%) of white crystalline **22**, m.p. 41 − 43 °C.

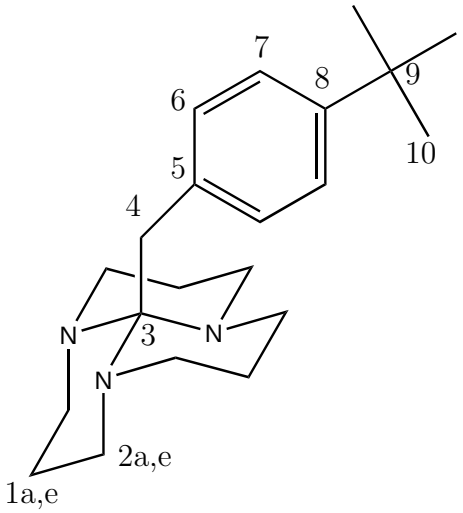
| $C_{21}H_{33}N_3$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 76.55 | 10.01 | 11.68 |
| Calc: | 77.01 | 10.16 | 12.83 |

**Infrared Spectrum** (KBr; $\nu$/cm$^{-1}$)

3092w, 3057w, 3029w, 2951s, 2924s, 2887m, 2840m, 2813m, 2760m, 2745m, 2707m, 2675m, 1888w, 1772m, 1700m, 1696m, 1685m, 1653m, 1635m, 1612m, 1602m, 1539w, 1514m, 1482m, 1461m, 1445m, 1436w, 1429w, 1411w, 1394w, 1381w, 1352m, 1346m, 1322m, 1311m, 1292m, 1274s, 1230m, 1212w,

1191w, 1176m, 1158m, 1123m, 1111m, 1101m, 1079m, 1047w, 1019, 1004w, 963s, 948m, 907w, 895w, 877m, 870m, 855w, 846w, 813s, 792w, 783w, 739w, 706w, 683w, 658w, 642m, 607m, 577w, 567w, 563w, 548w, 535w, 519w, 478w, 461w, 440w, 418w, 414w

**$^{1}$H and $^{13}$C NMR Data**




| $^{1}$H-**NMR** (200 MHz, $CDCl_3$) | | | | $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$) |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^{1}J_{HH}$(Hz) | | $\delta$(ppm) |
| 9 | | | | 34.19 |
| 3 | | | | 86.9 |
| 5-8 | 7.44-7.23 | | 5m | 147.43, 135.83 |
| | | | | 129.62, 124.44 |
| 4 | 3.32 | | 2s | 48.6 |
| 1a,e | 2.90 | - | 12m | 25.1 |
| 2a | 2.01 | - | 3m | 21.4 |
| 2e | 1.40 | - | 3m | 21.4 |
| 10 | 1.30 | - | 9s | 31.42 |

### 5.2.2 1,3,5-Trialkyl-1,3,5-triazacyclohexanes

1,3,5-Trimethyl-1,3,5-triazacyclohexane: **23**

**23** was prepared according to literature procedures [2] or more often obtained as byproduct in the synthesis of **31** and **45**. The crude **23** was after drying over sodium distilled *in vacuo* (60 °C/1.3 Pa) and stored under argon.

**Infrared Spectrum** (KBr; $\nu/cm^{-1}$)

2962s, 2938s, 2890s, 2841s, 2783s, 2769s, 2712s, 2662m, 2628m, 2596m, 2572m, 1470m, 1443m, 1427m, 1385s, 1372m, 1274m, 1262s, 1233s, 1158m, 1114s, 1049m, 1025m, 1003m, 913s, 859m

**$^1$H-NMR Data** (80 MHz; $CDCl_3$)

3.17 br (6H, $CH_2$), 2.28s (9H, Me)

**$^{13}$C-NMR Data** (50 MHz; $CDCl_3$)

77.12 ($CH_2$), 40.19 (Me)

1,3,5-Triethyl-1,3,5-triazacyclohexane: **24**

**$^1$H-NMR Data** (200 MHz; $CDCl_3$)

3.17 br (s, 6H, NC*H*$_2$N), 2.33 (q, J = 7.3 Hz, 6H, NC*H*Me), 0.93 (t, J = 7.3 Hz, 9H, NCH$_2$*Me*)

**$^1$H-NMR Data** (50 MHz; $CDCl_3$)

73.97 (NC*H*$_2$N), 46,30 (NC*H*$_2$CH$_3$), 12.50 (NCH$_2$*CH*$_3$)

1,3,5-Triisopropyl-1,3,5-triazacyclohexane: **25**

**24** and **25** were, except for the distillation temperature (68 − 80 °C/1.3 Pa, prepared analogous to **23**.

**$^1$H-NMR Data** (200 MHz; $CDCl_3$)

3.48 br (s, 6H, $CH_2$), 2.81 (septett, J = 6.59 Hz, 3H, $CHMe_2$, 1.02 (d, J = 6.5 Hz, 18 H, $CHMe_2$)

**$^{13}$C-NMR Data** (50 MHz; $CDCl_3$)

68.85 ($CH_2N$, 49.89 ($NCHMe_2$), 20.20 ($NCHMe_2$)

1,3,5-Tribenzyl-1,3,5-triazacyclohexane: **26**

**26** was prepared according to literature procedures [2].

**$^{1}$H-NMR Data** (270 MHz; $CDCl_3$)

3.44 br (6H, $NCH_2N$), 3.69s (6H, $PhCH_2$), 7.20-7.40m (m, 15H, $PhCH_2$

**$^{13}$C-NMR Data** (67.5 MHz; $CDCl_3$)

57.01 ($PhCH_2$), 73.73 ($NCH_2N$), 126.95 (p-$PhCH_2$), 128.18 (o,m-$PhCH_2$), 128.85 (o,m-$PhCH_2$), 128.42 (ipso-$PhCH_2$)

1,3,5-Tricyclohexyl-1,3,5-triazacyclohexane: **27**

**27** was prepared according to literature procedures [2].

**$^{1}$H-NMR Data** (200 MHz; $CDCl_3$)

3.59br (2H, N$CH_2$N), 2.98br (4H, N$CH_2$N), 2.67m (2H, NC*H*), 2.45m (1H, NC*H*), 1.59-1.93 (15H, Cy), 1.06-1.35 (15H, Cy)

**$^{13}$C-NMR Data** (50 MHz; $CDCl_3$)

68.23 (N$C$H$_2$N), 58.38 (N$C$H), 29.88, 26.12, 25.64 (Cy)

1,3,5-S-1-Phenyl-ethyl-1,3,5-triazacyclohexane: **28**

**28** was prepared according to literature procedures [12].

**Infrared Spectrum** (KBr; $\nu/cm^{-1}$)

3084m, 3060s, 3042m, 3026s, 3012s, 2974s, 2968s, 2929s, 2870s, 2823s, 2800s, 2784s, 2772s, 2754s, 2726m, 2710m, 2690m, 2672m, 2621m, 2555m, 1966m, 1953m, 1894m, 1881m, 1875m, 1829m, 1814m, 1802m, 1759m, 1602m, 1583m, 1491s, 1462s, 1452s, 1413m, 1393s, 1371s, 1361s, 1358s, 1348s, 1328m, 1314s, 1303s, 1295s, 1282s, 1211s, 1202s, 1185s, 1178s, 1159m, 1154s, 1140s, 1114s, 1103s, 1093s, 1080s, 1065s, 1062s, 1056s, 1037s, 1026s, 1008s, 999s,

983m, 976s, 957s, 945s, 911s, 847m, 839m, 784m, 778s, 767s, 763s, 758s, 704s, 700s, 612m, 601m, 580s, 550s, 544s, 528s, 517m

**$^1$H-NMR Data** (200 MHz; $CDCl_3$)

7.17-7.29m (15H, Ph), 3.72q (J = 6.7 Hz, 3H, PhMe*CH*N), 3.39br ($\Delta\nu_{1/2} \approx$ 19 Hz, 6H. N$CH_2$N, 1.29d (J = 6.7 Hz, 9H, Me)

**$^{13}$C-NMR Data** (50 MHz; $CDCl_3$)

144.28 (ipso-Ph), 128.06 (m,o-Ph), 127.31 (o,m-Ph), 126.68 (p-Ph), 69.98 (N$CH_2$N), 59.37 (NCN), 20.08 (Me)

1-Benzyl-3,5-dimethyl-1,3,5-triazacyclohexane: **29**

Benzylamine ($M$ = 107.2 gmol$^{-1}$, 9 ml, $\rho$ = 0.981, 82.4 mmol) and methylamine ($M$ = 31.1 gmol$^{-1}$, 100 ml, 40% in water, $\rho$ = 0.902, 1.2 mol) are dissolved in about 500 ml of ethanol. Paraformaldehyde ($M$ = 30.0 gmol$^{-1}$, 40 g, 1.33 mol) is added under rapid stirring. The reaction is finished, when the solution hascooled down to room temperature. The water and the ethanol are removed by rotary evaporation. Afterwards the remaining oil is distilled in vacuum ($80 - 90$ °C/1.3 Pa). The distillate is dissolved in pentane and stirred with sodium in an argon atmosphere for 48 h. The suspension is filtered and the solvent is removed in vacuum. 5 g (30%) of pure **29** ($M$ = 205.3 gmol$^{-1}$) remain as a colorless, oily liquid.

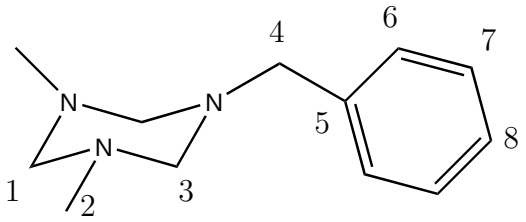
**Infrared Spectrum** (KBr/film; $\nu$/cm$^{-1}$)

3061s, 3027s, 2965m, 2939w, 2852s, 2838s, 2790w, 2726s, 2684s, 2642s, 2627s, 2601s, 1682s, 1605s, 1585s, 1495s, 1469m, 1453w, 1427s, 1418s, 1396s, 1384m, 1361m, 1311w, 1263w, 1234m, 1195s, 1144m, 1114m, 1076s, 1062s, 1050s, 1028m, 1009m, 1003m, 982s, 917m, 862s, 836s, 743m, 699m, 481m, 461m

**Mass Spectrum** (70 eV; 78 °C)

| m/z | $I_{relative}$% | fragment | m/z | $I_{relative}$% | fragment |
|---|---|---|---|---|---|
| 205 | (34) | $[\mathbf{29}]^+$ | 204 | (23) | $[\mathbf{29} - H]^+$ |
| 162 | (58) | $[\mathbf{29} - CH2N(CH3)]^+$ | 120 | (31) | $[PhCH_2NH = CH_2]^+$ |
| 91 | (88) | $[PhCH_2]^+$ | 44 | (100) | $[CH_3NCH_3]^+$ |

**$^1$H and $^{13}$C NMR Data**




$^1$H**-NMR** (200 MHz, $CDCl_3$)

| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | |
|---|---|---|---|---|
| 5-8 | 7.33-7.16 | - | 5m | 139.58, 128.44 |
| | | | | 128.03, 126.72 |
| 1+3 | 3.21 | - | br | 78.31, 74.66 |
| 4 | 3.70 | - | 2s | 56.56 |
| 2 | 2.17 | - | 6s | 39.86 |

$^{13}$C**-NMR** (50.29 MHz, $CDCl_3$)

1-Octyl-3,5-dimethyl-1,3,5-triazacyclohexane: **30**

Octylamine ($M$ = 129.2 gmol$^{-1}$, 9 ml, $\rho$=0.782, 54.5 mmol) and methylamine ($M$ = 31.1 gmol$^{-1}$, 100 ml, 40% in water, $\rho$=0.902, 1.2 mol) are dissolved in about 500 ml of ethanol. Paraformaldehyde ($M$ = 30.0 gmol$^{-1}$, 40 g, 1.33 mol) is added under rapid stirring. The reaction is finished, when the solution has cooled down to room temperature. The water and the ethanol are removed by rotary evaporation. Afterwards the remaining oil is distilled in vacuum (90 °C/1.3 Pa). The distillate is dissolved in pentane and stirred

with sodium under an argon atmosphere for 48 h. The suspension is filtered and the solvent is removed in vacuum. 8 g (65%) of pure **30** ($M$ = 227.4 gmol$^{-1}$) remain as a colorless, oily liquid.

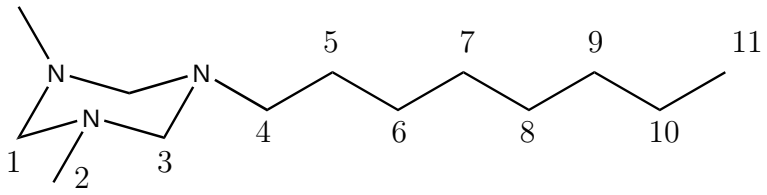
**Infrared Spectrum** (KBr/film; $\nu$/cm$^{-1}$)

2596m, 2626m, 2726m, 2786s, 2854s, 2927s, 2953s, 860m, 864m, 915m, 981s, 1003s, 1026m, 1049m, 1116s, 1147s, 1234m, 1262s, 1370m, 1385m, 1426w, 1444w, 1467m, 724m, 834m

**Mass Spectrum** (70 eV; 23 °C)

| m/z | $I_{relative}$% | fragment | m/z | $I_{relative}$% | fragment |
|---|---|---|---|---|---|
| 226 | (4) | $[\mathbf{30} - H]^+$ | 184 | (10) | $[\mathbf{30} - CH_3NCH_2]^+$ |
| 140 | (58) | $[\mathbf{30} - H(CH_2N(CH_3))_2]^+$ | 86 | (26) | $[H(CH_2N(CH_3))_2]^+$ |
| 85 | (18) | $[(CH_2N(CH_3))_2]^+$ | 44 | (100) | $[CH_3NCH_3]^+$ |

**$^1$H and $^{13}$C NMR Data**




$^1$H**-NMR** (200 MHz, $CDCl_3$)

| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) |
|---|---|---|
| 1+3 | 3.17 | - |
| 4 | 2.49 | 7 |
| 2 | 2.16 | - |
| 5-10 | 1.40-1.19 | - |
| 11 | 0.80 | 7 |

$^{13}$C**-NMR** (50.29 MHz, $CDCl_3$)

| | $\delta$(ppm) |
|---|---|
| br | 78.28, 75.15 |
| 2t | 52.52 |
| 6s | 39.99 |
| 12m | 31.63, 29.32, 29.09 |
| | 27.75, 27.18, 22.45 |
| 3t | 13.90 |

1-(1-Hydroxyethyl)-3,5-dimethyl-1,3,5-triazacyclohexane: **31**

**Method I:**

In about 80 ml $Me_3TAC$ **23** 1 ml ethanolamine ($M = 61.1$ gmol$^{-1}$, $\rho = 1.012$, 0.017 mol) is dissolved. The mixture is heated for 12 h at 130 °C. After removal of the $Me_3TAC$ in vacuum (60 °C/1.3 Pa) 2 g crude **31** ($M = 159.2$ gmol$^{-1}$) is obtained. For further purification **31** is dissolved in 10 ml methylamine (40% in water) and stirred for 12 h. The methylamine and the water are removed in vacuum. The remaining oil is transfered very quickly (Bunsen burner) in vacuum in a liquid nitrogen cooled flask. Yield 1.2 g (44%).

**Method II:**

Ethanolamine ($M = 61.1$ gmol$^{-1}$, 9 ml, $\rho = 1.012$, 0.15 mol) and methylamine ($M = 107.2$ gmol$^{-1}$, 100 ml, 40% in water, $\rho = 0.902$, 1.2 mol) are dissolved in about 200 ml of ethanol. Paraformaldehyde ($M = 30.0$ gmol$^{-1}$, 40 g, 1.33 mol) is added under rapid stirring. The reaction is finished, when the solution has cooled down to room temperature. Water and ethanol are removed by rotary evaporation. **31** is, together with **23**, extracted from $Me(EtOH)_2TAC$ and $(EtOH)_3TAC$ with pentane. The pentane is removed by rotary evaporation, the remaining **23** is removed *in vacuo* at 60 °C/1.3 Pa. The crude product can be purified by column chromatography on silica gel ($CH_2Cl_2$:$Et_3N$=1:1). Yield: 1.2 g (50%).

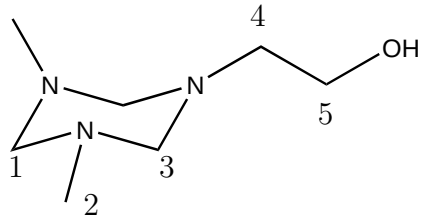
Using both methods the resulting **31** is contaminated by about 5-6% **23**. Due to the equilibrium between $Me(EtOH)_2TAC$, $Me_3TAC$ and $Me_2(EtOH)TAC$ it is difficult to obtain pure **31**. It should be prepared directly prior use or stored refrigerated.

**Infrared Spectrum** (KBr/film; $\nu$/cm$^{-1}$)

3226w, 2941s, 2899s, 2856s, 2789s, 2729w, 2687w, 2650w, 2604w, 1468m,

1445m, 1429m, 1385s, 1335w, 1258s, 1234s, 1203w, 1147s, 1108s, 1055w, 1034w, 1003s, 983w, 961w, 944w, 917s, 899s, 862m, 837w, 795w, 655w, 616w

### $^{1}$H and $^{13}$C NMR Data




$^{1}$H-**NMR** (200 MHz, $CDCl_3$) $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$)

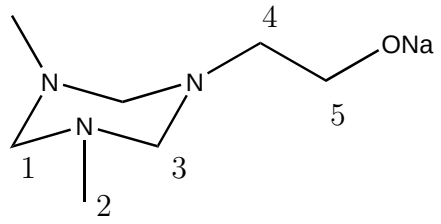
| Assignment | $\delta$(ppm) | $^{1}J_{HH}$(Hz) | | $\delta$(ppm) |
|---|---|---|---|---|
| O**H** | 5.35 | - | br | |
| 1+3 | 3.14 | - | br | 79.55, 73.71 |
| 5 | 3.61 | 5.16 | 2t | 59.77 |
| 4 | 2.89 | 5.16 | 2t | 57.27 |
| 2 | 2.06 | - | 6s | 39.02 |

1-(1-Sodiumethanolato)-3,5-dimethyl-1,3,5-triazacyclohexane: **32**

6 g of **31** ($M = 159.2\ \mathrm{gmol^{-1}}$, 37.7 mmol) is dissolved in 100 ml of pentane. Several small pieces of sodium are added and the mixture is stirred for 12 hour at room temperature. After cooling down to about $-30$ °C, a dirty gray solid precipitates which is filtered off, along with the remaining sodium. After removal of the solvent 5 g of **32** ($M = 181.2\ \mathrm{gmol^{-1}}$, 73%) is obtained as a light yellow waxy solid.

The $Me_2$(EtONa)TAC can be heated to at least 70 °C without signs of the equilibrium of the free alcohol.

**$^1$H and $^{13}$C NMR Data**




| $^1$H-**NMR** (400 MHz, $D_2O$) | | | | $^{13}$C-**NMR** (100.61 MHz, $D_2O$) |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
| 5 | 3.60 | 6.0 | 2t | 58.42 |
| 1,3 | 3.14 | - | br | 76.03, 72.49 |
| 4 | 2.60 | 6.0 | 2t | 53.35 |
| 2 | 1.93 | - | 6s | 38.48 |

1-(1-Cyanoethyl)-3,5-dimethyl-1,3,5-triazacyclohexane: **33**

**Method I:**

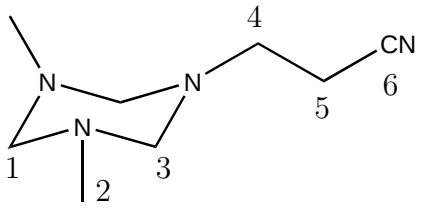
In about 80 ml of $Me_3$TAC **23** 1 ml 3-aminopropionitrile ($M = 70.1$ gmol$^{-1}$, $\rho = 0.988$, 14.4 mmol) is dissolved. The mixture is heated for 12 h at 130 °C. After removal of the $Me_3$TAC in vacuum (60 °C/1.3 Pa) 2.4 g crude **33** is obtained. For further purification **33** is dissolved in 50 ml of ether and filtered through a short column filled with silica gel. The ether is removed *in vacuo*. 2.1 g of **33** ($M = 168.2$ gmol$^{-1}$) as a colorless, oily liquid is obtained. Yield: (87%).

**Method II:**

3-Aminopropionitrile ($M = 70.1$ gmol$^{-1}$, 9 ml, $\rho = 0.988$, 0.13 mol) and methylamine ($M = 31.1$ gmol$^{-1}$, 100 ml, 40% in water, $\rho = 0.902$, 1.2 mol) are dissolved in about 200 ml of ethanol. Paraformaldehyde ($M = 30.0$ gmol$^{-1}$, 40 g, 1.33 mol) is added under rapid stirring. The reaction is finished, when

the solution has cooled down to room temperature. The solvents are removed by rotary evaporation. Purification analogous to method I. Yield: 20 g (91%).

**$^1$H and $^{13}$C NMR Data**




| $^1$H-**NMR** (200 MHz, $CDCl_3$) | | | | $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$) |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
| **C**N | - | - | - | 118.82 |
| 1+3 | 3.91 | - | br | 74.30, 78.75 |
| 5 | 2.91 | 6.9 | 2t | 48.36 |
| 4 | 2.36 | 6.9 | 2t | 39.63 |
| 2 | 2.03 | - | 6s | 17.67 |

1-(1-Hydroxyethyl)-3,5-diethyl-1,3,5-triazacyclohexane: **34**

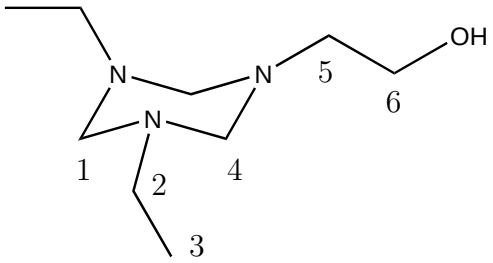
**Method I:**

In about 80 ml of $Et_3$TAC **24** 1 ml of ethanolamine ($M = 61.1$ gmol$^{-1}$, $\rho = 1.012$, 16.6 mmol) is dissolved. The mixture is heated for 12 h at 130 °C. After removal of the $Et_3$TAC in vacuum (70 °C/1.3 Pa) 1.9 g of crude **34** is obtained. For further purification **34** is dissolved in ethylamine (10 ml, 70% in water) and stirred for 12 h. Ethylamine and water are removed in vacuum. The remaining oil is very quickly (Bunsen burner) distilled in vacuum. Yield 1.4 g ($M = 187.3$ gmol$^{-1}$, 45%).

**Method II:**

Ethanolamine ($M = 61.1\ \mathrm{gmol^{-1}}$, 9 ml, $\rho = 1.012$, 14.9 mmol) and aqueous ethylamine ($M = 45.1\ \mathrm{gmol^{-1}}$, 100 ml, 70%, $\rho = 0.796$, 1.2 mol) are dissolved in about 200 ml of ethanol. Paraformaldehyde ($M = 30.0\ \mathrm{gmol^{-1}}$, 40 g, 1.33 mol) is added under rapid stirring. The reaction is finished, when the solution has cooled down to room temperature. The water and the ethanol are removed by rotary evaporation. The remaining oil is dissolved in 40 ml of methanol and 20 ml of pentane. While the solution cooles down to −78 °C two phases form. The lighter pentane phase contains mainly **24** and the desired product **31**. This procedure is repeated several times. After removal of the pentane **24** is removed *in vacuo* (60 °C/1.3 Pa). Further purification can be achieved by column chromatography on silica gel ($CH_2Cl_2/Et_3N$ = 1:1). Yield 13 g (47%) of colorless, oily **34**.

**$^1$H and $^{13}$C NMR Data**



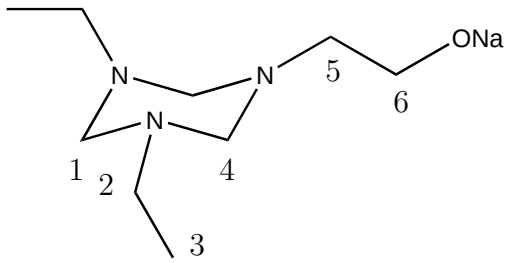

| $^1$H-**NMR** (200 MHz, $CDCl_3$) | | | | $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$) |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
| O**H** | 5.74 | - | br | |
| 6 | 3.62 | 4.7 | 2t | 60.22 |
| 1+4 | 3.29 | - | br | 75.36, 72.87 |
| 5 | 2.85 | 4.7 | 2t | 58.03 |
| 2 | 2.24 | 7.3 | 4q | 46.27 |
| 3 | 0.99 | 7.3 | 6t | 12.24 |

1-(1-Sodiumethanolato)-3,5-diethyl-1,3,5-triazacyclohexane: **35**

6 g of **34** ($M = 187.3\ \mathrm{gmol^{-1}}$, 32.0 mmol) is dissolved in 100 ml of pentane. Several small pieces of sodium are added and the mixture is stirred for 12 hour at room temperature. After cooling down to about $-30\ ^\circ\mathrm{C}$, a dirty gray solid precipitates which is filtered off along with the remaining sodium. After removal of the solvent 3 g of **35** ($M = 209.3\ \mathrm{gmol^{-1}}$, 45%) is obtained as a deep orange, waxy solid.

The $Et_2$(EtONa)TAC can be heated to at least 70 °C without signs of the equilibrium of the free alcohol.

**$^1$H and $^{13}$C NMR Data**




| $^1$H-**NMR** (200 MHz, $D_2O$) | | | | $^{13}$C-**NMR** (50.29 MHz, $D_2O$) |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
| 6 | 3.49 | 5.6 | 2t | 58.52 |
| 1,4 | 3.24 | - | br | 71.80, 71.54 |
| 5 | 2.54 | 5.6 | 2t | 53.78 |
| 2 | 2.33 | 7.3 | 49 | 45.92 |
| 3 | 0.87 | 7.3 | 6t | 10.61 |

1-(1-Cyanoethyl)-3,5-diethyl-1,3,5-triazacyclohexane: **36**

**Method I:**

In about 80 ml of $Et_3TAC$ **24** 1 ml 3-aminopropionitile ($M = 70.1$ gmol$^{-1}$, $\rho$ = 0.988, 14.1 mmol) is dissolved. The mixture is heated for 12 h at 130 °C. After removal of the $Et_3TAC$ in vacuum (60 °C/1.3 Pa) 2.4 g crude **36** is obtained. For further purification the **36** is dissolved in 50 ml of ether and filtered through a short column filled with silica gel. The ether is removed *in vacuo*. 2.1 g of **36** as a colorless oily liquid is obtained. Yield: ($M$ = 196.3 gmol$^{-1}$, 76%).

**Method II:**

3-Aminopropionitrile ($M = 70.1$ gmol$^{-1}$, 9 ml, $\rho = 0.988$, 0.13 mol) and ethylamine (100 ml, 40% in water, $\rho$ = 0.902, 1.2 mol) are dissolved in about 200 ml of ethanol. Paraformaldehyde (40 g, 1.33 mol) is added under rapid stirring. The reaction is finished, when the solution hascooled down to room temperature. The water and the ethanol are removed by rotary evaporation. Purification analoguos to method I. Yield: 20 g (78%).

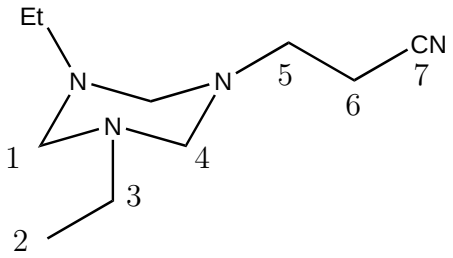
**Infrared Spectrum** (KBr/film; $\nu$/cm$^{-1}$)

2969s, 2936s, 2874s, 2806s, 2790s, 2642m, 2247m, 1470s, 1454s, 1379m, 1356m, 1292s, 1215m, 1189m, 1146w, 1122m, 1104m, 1045s, 1008s, 805m, 649m

**Mass Spectrum** (70 eV; 80 °C)

| m/z | $I_{relative}$% | fragment |
|---|---|---|
| 196 | (8) | $[\mathbf{33}]^+$ |
| 139 | (27) | $[\mathbf{33} - CH_3CH_2NCH_2]^+$ |
| 114 | (18) | $[\mathbf{33} - NCCH_2CH_2N = CH_2]^+$ |
| 99 | (27) | $[(CH_3CH_2N)_2 - H]^+$ |

**$^1$H and $^{13}$C NMR Data**

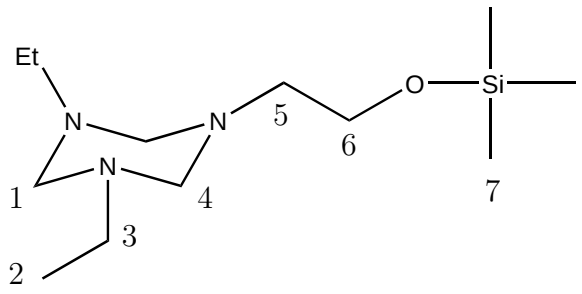



| $^1$H-**NMR** (200 MHz, $CDCl_3$) | | | | $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$) |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
| **C**N | - | - | - | 118.66 |
| 1+4 | 3.286, 3.16 | - | br | 74.48, 73.07 |
| 5 | 2.861 | 7 | 2t | 48.26 |
| 6 | 2.375 | 7 | 2t | 46.09 |
| 3 | 2.246 | 7 | 4q | 17.47 |
| 2 | 0.947 | 7 | 6t | 12.12 |

1-(1-Ethoxytrimethylsilyl)-3,5-diethyl-1,3,5-triazacyclohexane: **37**

6 g of **34** ($M = 187.3$ gmol$^{-1}$, 32.0 mmol) are dissolved in a mixture of 200 ml of pentane and 100 ml of triethylamine. Under rapid stirring $Me_3SiCl$ ($M = 108.6$ gmol$^{-1}$, $\rho = 0.856$, 4 ml, 36.8 mmol) is added. At once a heavy white precipitate of $Et_3N \cdot HCl$ forms. After stirring at room temperature for 2 h the $Et_3N \cdot HCl$ is filtered off and remaining product extracted with about 200 ml of pentane. The solvents are removed *in vacuo* yielding 7 g of crude yellow **37** ($M = 259.5$ gmol$^{-1}$, 84%).

**$^1$H and $^{13}$C NMR Data**

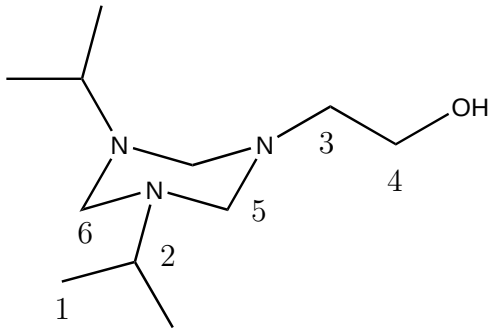



| $^1$H-**NMR** (400 MHz, $CDCl_3$) | | | | $^{13}$C-**NMR** (100.61 MHz, $CDCl_3$) |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
| 6 | 3.70 | 6.4 | 2t | 61.34 |
| 1+4 | 3.40 | - | br | 74.34, 74.12 |
| 5 | 2.70 | 6.4 | 2t | 54.78 |
| 3 | 2.46 | 7.3 | 4q | 46.32 |
| 2 | 1.09 | 7.3 | 6t | 12.43 |
| 7 | 0.13 | - | 9s | -0.70 |

1-(1-Hydroxyethyl)-3,5-diisopropyl-1,3,5-triazacyclohexane: **38**

Ethanolamine ($M$ = 61.1 gmol$^{-1}$, 9 ml, $\rho$ = 1.012, 0.15 mol) and isopropylamine ($M$ = 59.1 gmol$^{-1}$, 100 ml, $\rho$ = 0.694, 1.2 mol) are dissolved in about 200 ml of ethanol. Paraformaldehyde ($M$ = 30.0 gmol$^{-1}$, 40 g, 1.33 mol) is added under rapid stirring. The reaction is finished, when the solution has cooled down to room temperature. The water and the ethanol are removed by rotary evaporation. Purification analogous to **31** and **34** yields 11 g of **38** ($M$ = 215.3 gmol$^{-1}$, 35%) as colorless oil.

**$^1$H and $^{13}$C NMR Data**

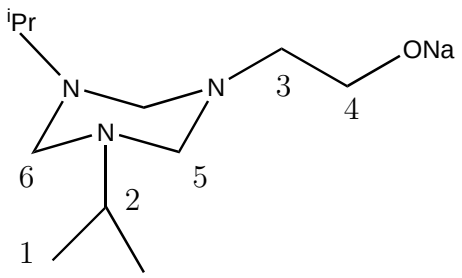



| $^1$H-**NMR** (200 MHz, $CDCl_3$) | | | | $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$) |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
| O**H** | 5.7 | - | br | |
| 4 | 3.64 | 4.7 | 2t | 59.99 |
| 5+6 | 3.48 | - | br | 68.89, 69.51 |
| 3 | 2.86 | 4.7 | 2t | 58.13 |
| 2 | 2.64 | 6.5 | 2sp | 50.58 |
| 1 | 1.00 | 6.5 | 12d | 19.04 |

1-(1-Sodiumethoxy)-3,5-diisopropyl-1,3,5-triazacyclohexane: **39**

2 g of **38** ($M$ = 215.3 gmol$^{-1}$, 9.3 mmol) is dissolved in 100 ml of pentane. Several small pieces of sodium are added and the mixture is stirred for 12 hour at room temperature. After cooling down to about −30 °C, a dirty gray solid precipitates which is filtered off along with the remaining sodium. After removal of the solvent in vacuum 1.4 g of **35** ($M$ = 237.3 gmol$^{-1}$, 64%) are obtained as a yellow, waxy solid.

**$^1$H and $^{13}$C NMR Data**




$^1$H-**NMR** (200 MHz, $CDCl_3$) $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$)

| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
|---|---|---|---|---|
| 4 | 3.79 | 4.7 | 2t | 58.89 |
| 5+6 | 3.74 | - | br | 67.82, 66.99 |
| 3 | 3.11 | 4.7 | 2t | 57.23 |
| 2 | 2.59 | 6.5 | 2sp | 48.66 |
| 1 | 1.10 | 6.5 | 12d | 19.00 |

1-(1-Hydroxypropyl)-3,5-dimethyl-1,3,5-triazacyclohexane: **40**

**Method I:**

In about 80 ml of $Me_3$TAC propanolamine ($M$ = 75.1 gmol$^{-1}$, 1 ml, $\rho$ = 0.982, 0.013 mol) is dissolved. The mixture is heated for 12 h at 130 °C. After removal of the $Me_3$TAC in vacuum (60 °C/1.3 Pa) 1.3 g crude **40** is obtained. For further purification **40** is dissolved in 10 ml of methylamine (40% in water) and stirred for 12 h. The methylamine and the water are removed in vacuum. The remaining oil is transfered very quickly (Bunsen burner) in vacuum in a with liquid nitrogen cooled flask. Yield 1.0 g ($M$ = 156.3 gmol$^{-1}$, 49%).

**Method II:**

Propanolamine ($M$ = 75.1 gmol$^{-1}$, 9 ml, $\rho$ = 0.982, 0.12 mol) and methylamine ($M$ = 31.1 gmol$^{-1}$, 100 ml, 40% in water, $\rho$ = 0.902, 1.2 mol) are

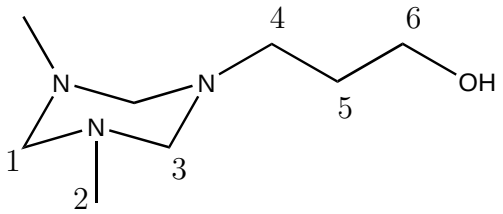
dissolved in about 500 ml of ethanol. Paraformaldehyde ($M = 30.0\ \mathrm{gmol^{-1}}$, 40 g, 1.33 mol) is added under rapid stirring. The reaction is finished, when the solution has cooled down to room temperature. The solvents are removed by rotary evaporation. **40** is, along with $Me_3TAC$, extracted from $Me(PrOH)_2TAC$ and $(PrOH)_3TAC$ with cooled pentane. The pentane is removed by rotary evaporation, and the remaining $Me_3TAC$ is removed *in vacuo* at 60 °C/1.3 Pa. The crude product can be purified by column chromatography on silica gel ($CH_2Cl_2$:$Et_3N$=1:1). Yield: 10.2 g ($M = 156.3\ \mathrm{gmol^{-1}}$, 55%).

With both methods the resulting **40** is contaminated by about 5-6% $Me_3TAC$. Due to an equilibrium between $Me(PrOH)_2TAC$, $Me_3TAC$ and $Me_2PrOHTAC$ it is difficult to obtain pure **40**. It should be prepared directly prior use or stored refrigerated.

**Infrared Spectrum** (KBr/film; $\nu/\mathrm{cm^{-1}}$)

3282s, 2940s, 2860s, 2786s, 2729m, 2645m, 2602w, 2512w, 2458w, 1675w, 1465s, 1447s, 1428s, 1385s, 1371s, 1347m, 1316w, 1261s, 1233s, 1193m, 1147s, 1116s, 1062s, 1050s, 1006s, 982m, 946w, 917s, 900m, 861m, 770w, 652w, 624w, 558w, 537w, 493w, 457w, 443w, 433w, 418w, 407w

**$^1$H and $^{13}$C NMR Data**

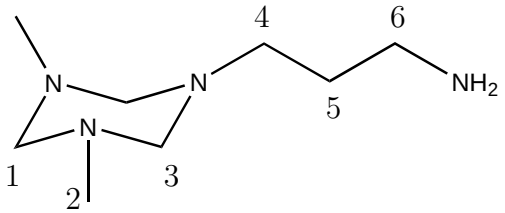


| $^1$H-**NMR** (200 MHz, $CDCl_3$) | | | | $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$) |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
| O**H** | 4.51 | - | br | |
| 4 | 3.59 | 5.16 | 2t | 62.82 |
| 1+3 | 3.06 | - | br | 77.41, 74.92 |
| 6 | 2.54 | 5.16 | 2t | 51.51 |
| 2 | 2.11 | - | 6s | 39.85 |
| 5 | 1.53 | 5.16 | 2p | 29.37 |

1-(1-Amio-propyl)-3,5-dimethyl-1,3,5-triazacyclohexane: **41**

2 g of $Me_2$(EtCN)TAC ($M$ = 168.2 gmol$^{-1}$, 11.89 mmol) are dissolved in about 10 ml of ethanol. 5 g of an aqueous (50%) Raney nickel suspension is added. Under rapid stirring and water cooling 0.9 g of $NaBH_4$ ($M$ = 37.8 gmol, 23.78 mmol) in 5 ml of an 8 normal NaOH solution is added dropwise to the mixture. After 5 minutes the reaction is finished. The Raney nickel is filtered off. After removal of the ethanol in vacuum, about 2 g of KOH are added to the mixture and the product is extracted with hexane. Yield: 1.13 g ($M$ = 172.2 gmol$^{-1}$, 55%) of colorless, oily **41**.

**$^1$H and $^{13}$C NMR Data**

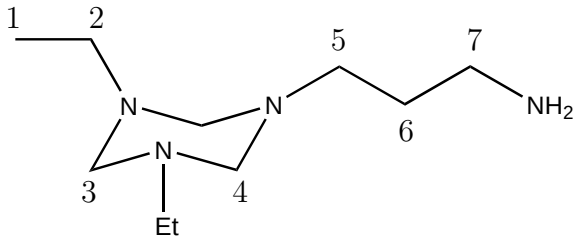


| $^1$H-**NMR** (200 MHz, $CDCl_3$) | | | | $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$) |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
| 1+3 | 3.01 | - | br | 78.09, 75.09 |
| 6 | 2.50 | 6.9 | 2t | 50.12 |
| 4 | 2.38 | 6.9 | 2t | 40.28 |
| 2 | 1.98 | - | 12s | 40.05 |
| 5 | 1.35 | 6.9 | 2q | 31.26 |

1-(1-Amio-propyl)-3,5-diethyl-1,3,5-triazacyclohexane: **42**

**42** was prepared analogous to **41**. 2 g of $Et_2$(EtCN)TAC ($M = 196.3$ gmol$^{-1}$, 10.18 mmol), 5 g of a Raney nickel suspension, 1.1 g of $NaBH_4$ ($M = 37.8$ gmol$^{-1}$, 29.07 mmol) were used. Yield: 1.10 g ($M = 200.3$ gmol$^{-1}$, 54%) of **42**.

**$^1$H and $^{13}$C NMR Data**




| $^1$H-**NMR** (200 MHz, $CDCl_3$) | | | | $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$) |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
| 3+4 | 3.11 | - | br | 73.63, 74.00 |
| 7 | 2.54 | 6.9 | 2t | 50.21 |
| 2+5 | 2.27 | 6.9 | 6m | 46.30, 40.32 |
| 6 | 1.40 | - | 2q | 31.12 |
| 1 | 1.35 | 6.9 | 6t | 12.50 |

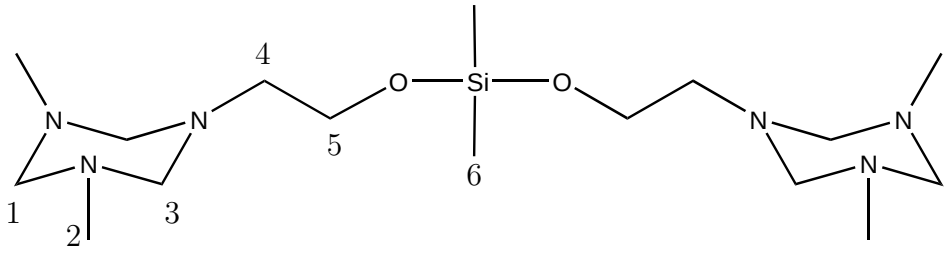
Di-methyl-di-(1-ethyl-3,5-dimethyl-1,3,5-triazacyclohexyl)-siloxane : **43**

8 g of $Me_2$(EtOH)TAC ($M$ = 159.2 gmol$^{-1}$, 50.24 mmol) are dissolved in a mixture of 150 ml of pentane and 200 ml of $Et_3N$. Under rapid stirring 3.5 ml of freshly distilled $Me_2SiCl_2$ ($M$ = 129.1 gmol$^{-1}$, $\rho$ = 1.064, 28.84 mmol) are added. At once a voluminous precipitate forms. The suspension is stirred for 15 minutes at room temperature. Afterwards the solid is filtered off and the product extracted with pentane. After evaporation of the pentane the remaining colorless oil is heated for 30 minutes at 80 °C in vacuum to remove volatile parts. Further purification is not necessary. Yield: 8.6 g ($M$ = 361.5 gmol$^{-1}$, 95%) of pure colorless, oily **43**.

**Mass Spectrum** (70 eV; 43 °C)

| m/z | $I_{relative}$% | fragment |
|---|---|---|
| 374 | (0.8) | [**43**]$^+$ |
| 331 | (0.7) | [**43** − $CH_3NCH_2$]$^+$ |
| 318 | (0.4) | [**43** − $CH_3NCH_2NH$]$^+$ |
| 287 | (2.3) | [**43** − $CH_3NCH_2N(CH_3)NH_2$]$^+$ |
| 244 | (3.8) | [**43** − $Me_3$TAC]H$^+$ |
| 130 | (66) | $Me_3$TAC+H$^+$ |

**$^1$H and $^{13}$C NMR Data**

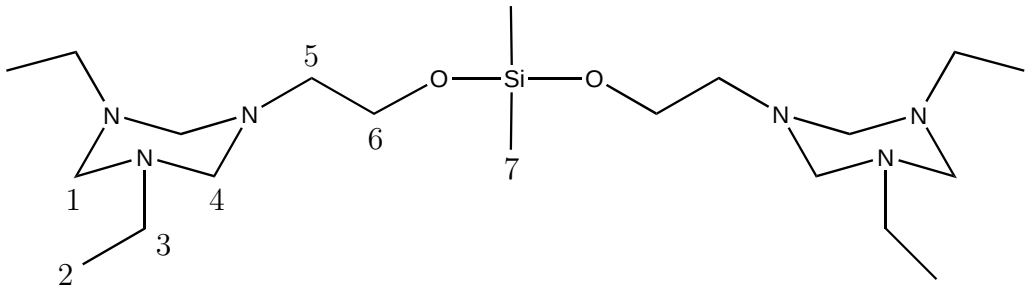


| $^1$H-**NMR** (200 MHz, $CDCl_3$) | | | | $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$) |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
| 5 | 3.65 | 6.9 | 4t | 61.21 |
| 1+3 | 3.08 | - | br | 78.41, 75.42 |
| 4 | 2.74 | 6.9 | 4t | 54.69 |
| 2 | 2.13 | - | 12s | 39.92 |
| 6 | 0.03 | - | 6s | -3.28 |

Di-ethyl-di-(1-ethyl-3,5-dimethyl-1,3,5-triazacyclohexyl)-siloxane : **44**

**44** was prepared analogue to **43**. 6 g of $Et_2$(EtOH)TAC ($M = 187.3$ gmol$^{-1}$, 32.03 mmol), 2 ml of $Me_2SiCl_2$ (($M = 129.1$ gmol$^{-1}$, $\rho = 1.064$, 16.48 mmol) were used. Yield: 5.8 g ($M = 430.7$ gmol$^{-1}$, 84%) of pure colorless, oily **44**.

**$^1$H and $^{13}$C NMR Data**



| $^1$H-**NMR** (400 MHz, $CDCl_3$) | | | | $^{13}$C-**NMR** (100.63 MHz, $CDCl_3$) |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
| 6 | 3.62 | 6.9 | 4t | 46.39 |
| 1+4 | 3.32 | - | br | 74.20, 74.41 |
| 3 | 2.38 | 6.4 | 8q | 61.42 |
| 2 | 1.00 | 6.9 | 12t | 12.52 |
| 5 | 2.61 | 6.4 | 4t | 54.86 |
| 7 | 0.06 | - | 6s | -0.63 |

### 5.2.3 1,3-Di-(1-methylene-3,5-dialkyl-1,3,5-triazacyclohexyl)-benzenes

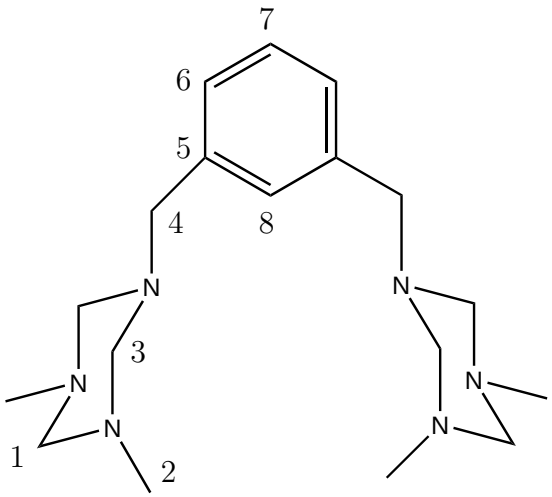
1,3-Di-(1-methylene-3,5-dimethyl-1,3,5-triazacyclohexyl)-benzene: **45**

100 ml of methylamine ($M = 31.1$ gmol$^{-1}$, 40% in water, $\rho = 0.902$, 1.2 mol) and 9 ml of m-xylylamine ($M = 136.2$ gmol$^{-1}$, $\rho = 1.032$, 68.2 mmol) are dissolved in 150 ml of ethanol. Under vigorous stirring and water cooling 40 g of paraformaldehyde ($M = 30.0$ gmol$^{-1}$, 1.33 mol) are added. The reaction is finished when all of the formaldehyde is dissolved and the mixture has cooled down to room temperature. The solvent and the also formed $Me_3$TAC were evaporated in vacuum (70 °C/1.3 Pa). The remaining colorless oily liquid is heated with the flame of a Bunsen burner under vacuum until the oil starts to smoke. 18 g of crude yellow **45** is obtained and solved in about 50 ml of ether and filtered through a short column of neutral $Al_2O_3$. For drying the solution is stirred with sodium over night. After filtering through alumina again and removal of the solvent 16.3 g **45** ($M = 332.4$ gmol$^{-1}$, 0.05 mol, 72%) is yielded as a colorless highly viscose oil.

**Mass Spectrum** (70 eV; 109 °C)

| m/z | $I_{relative}$% | fragment |
|---|---|---|
| 332 | (12) | $[\mathbf{45}]^+$ |
| 289 | (7) | $[\mathbf{45} - CH_3NCH_2]^+$ |
| 274 | (9) | $[\mathbf{45} - CH_2 = N = CH_2NH_2]^+$ |
| 245 | (65) | $[\mathbf{45} - 2 \cdot CH_3NCH_2]^+$ |
| 217 | (60) | $[\mathbf{45} - H - (CH_3)_2TAC]^+$ |
| 203 | (35) | $[\mathbf{45} - H - (CH_3)_2TACCH_2]^+$ |
| 161 | (53) | $[CH_2 = NCH_2C_6H_4CH_2NH = CH_2]^+$ |
| 33 | (28) | $[PhCH_2NHCH_2]^+$ |
| 105 | (35) | $[\mathbf{45} - H - 2 \cdot (CH_3)_2TAC]^+$ |

**$^1$H and $^{13}$C NMR Data**



| $^1$H-**NMR** (200 MHz, $CDCl_3$) | | | | $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$) |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
| 5,6,7,8 | 7.3-7.1 | - | 4m | 143.28, 128.28 |
| | | | | 125.39, 125.09 |
| 4 | 3.83 | - | 4s | 46.09 |
| 1,3 | 3.18 | - | 3br | 76.86, 74.55 |
| 2 | 1.49 | - | 12s | 39.91 |

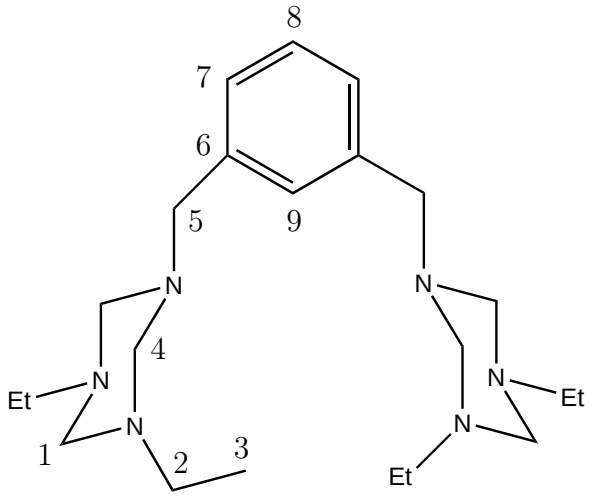
1,3-Di-(1-methylene-3,5-diethyl-1,3,5-triazacyclohexyl)-benzene: **46**

95 ml of ethylamine ($M = 45.1$ gmol$^{-1}$, 70% in water, $\rho = 0.796$, 1.13 mol) and 9 ml of m-xylylamine ($M = 136.2$ gmol$^{-1}$, $\rho = 1.032$, 68.2 mmol) are dissolved in 150 ml of ethanol. Under vigorous stirring and water cooling 39.3 g of paraformaldehyde ($M = 30.0$ gmol$^{-1}$, 1.31 mol) is added. The reaction is finished when all of the formaldehyde is dissolved and the mixture has cooled down to room temperature. The solvent and the byproduct $Et_3TAC$ were evaporated in vacuum (70 °C/1.3 Pa). The remaining colorless oily liquid is heated with the flame of a Bunsen burner in vacuum until it begins to smoke. 25 g of crude yellow **46** is obtained, solved in about 50 ml of ether and filtered through a short column of neutral $Al_2O_3$. For drying the solution is stirred with sodium over night. After filtering through alumina again and removal of the solvent 22 g of **46** ($M = 388.5$ gmol$^{-1}$, 0.06 mol, 83%) is yielded as a colorless highly viscose oil.

**Infrared Spectrum** (KBr/film; $\nu$/cm$^{-1}$)

3201w, 3101w, 3057w, 3025w, 2967s, 2935s, 2869s, 2795s, 2645s, 2458w, 2253w, 1943w, 1877w, 1683s, 1609m, 1590w, 1486m, 1471s, 1452s, 1397s, 1378s, 1354s, 1292s, 1212s, 1173s, 1146s, 1103s, 1066s, 1040m, 1011m, 993s, 913s, 863s, 791m, 756m, 704m, 664m, 621w, 519w, 489w, 438w

**$^{1}$H and $^{13}$C NMR Data**




| $^{1}$H-**NMR** (200 MHz, $CDCl_3$) | | | | $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$) |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^{1}J_{HH}$(Hz) | | $\delta$(ppm) |
| 6,7,8,9 | 7.1-6.7 | - | 4m | 138.3, 128.8, 127.8, 127.1 |
| 5 | 3.60 | - | 4s | 56.58 |
| 1,4 | 3.29 | - | br | 73.88, 73.37 |
| 3 | 0.99 | 7.3 | 12t | 12.30 |
| 2 | 2.42 | 7.3 | 8q | 46.20 |

1,3-Di-(1-methylene-3,5-diisopropyl-1,3,5-triazacyclohexyl)-benzene) : **47**

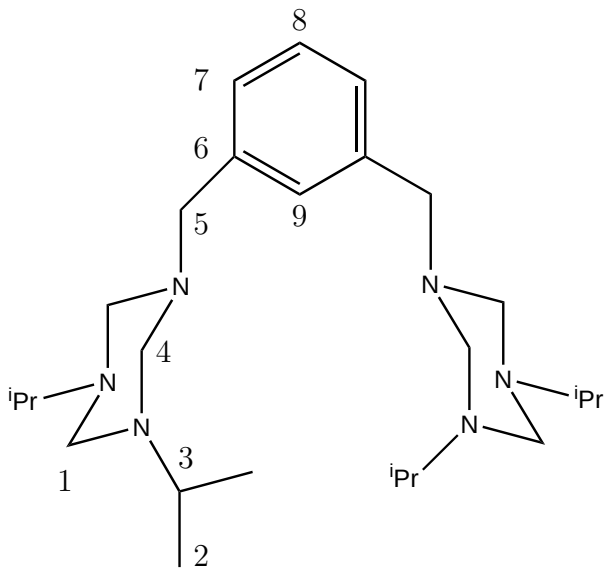
100 ml of isopropylamine ($M = 59.1$ gmol$^{-1}$, $\rho = 0.694$, 1.2 mol) and 9 ml of m-xylylamine ($M = 136.2$ gmol$^{-1}$, $\rho = 1.032$, 68.2 mmol) are dissolved in 200 ml of ethanol. Under vigorous stirring and water cooling paraformaldehyde ($M = 30.0$ gmol$^{-1}$, 40 g, 1.33 mol) is added. The reaction is finished when all of the formaldehyde is dissolved and the mixture has cooled down to room temperature. The solvent and the mainly formed $^{i}Pr_3TAC$ were evaporated in vacuum (70 °C/1.3 Pa). The remaining light yellow, oily liquid

is heated with the flame of a Bunsen burner in vacuum until it begins to smoke. 22 g of a crude yellow **47** is obtained and dissolved in about 50 ml of ether and filtered through a short column of neutral $Al_2O_3$. For drying the solution is stirred with sodium over night. After filtering through alumina again and removal of the solvent 17 g of **47** ($M = 444.7\ \mathrm{gmol}^{-1}$, 38.2 mmol, 56%) is yielded as a colorless highly viscose oil.

**Infrared Spectrum** (KBr/film; $\nu/\mathrm{cm}^{-1}$)

3178w, 2965s, 2929s, 2872s, 2814s, 2647m, 2455w, 1939w, 1876w, 1805w, 1682w, 1650w, 1609w, 1590w, 1463m, 1407m, 1381s, 1362s, 1329s, 1239s, 1212s, 1187s, 1166s, 1143m, 1116m, 1071m, 1007s, 971m, 915m, 892m, 853w, 789w, 754w, 704w, 676w, 621w, 547w, 515w, 453w, 450w, 446w, 442w, 439w, 435w, 414w

**$^1$H and $^{13}$C NMR Data**



| $^1$H-**NMR** (200 MHz, $CDCl_3$) | | | | $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$) |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
| 6,7 | 7.4-7.2 | - | 4m | 135.4, 129.3 |
| 8,9 | | | | 127.9, 127.4 |
| 5 | | | 4m | 56.94 |
| 1 | 3.64 | - | 4m | 68.34 |
| 4 | 3.47 | - | 8br | 71.15 |
| 3 | 2.91 | 6.4 | 4sp | 49.80 |
| 2 | 1.07 | 6.4 | 24d | 19.72 |

1,3-Di-(1-methylene-3,5-tert-butyl-1,3,5-triazacyclohexyl)-benzene: **48**

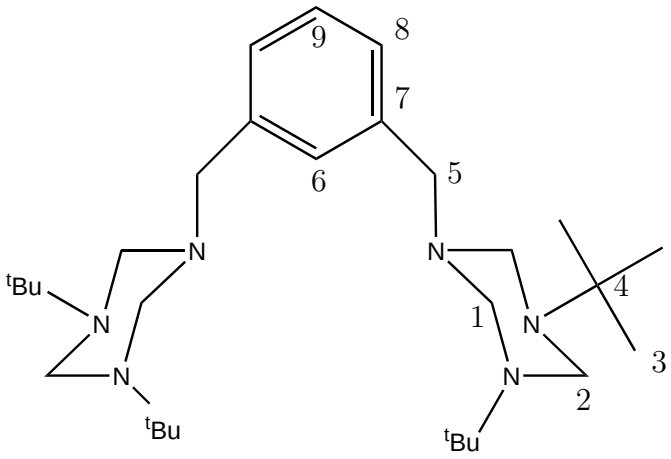
100 ml of $^t$butyl-amine ($M = 73.1$ gmol$^{-1}$, $\rho = 0.696$, 0.95 mol) and 9 ml of m-xylylamine ($M = 136.2$ gmol$^{-1}$, $\rho = 1.032$, 68.2 mmol) are dissolved in 500 ml of ethanol. Under vigorous stirring and water cooling paraformaldehyde ($M = 30.0$ gmol$^{-1}$, 40 g, 1.33 mol) is added. The reaction is finished when all of the formaldehyde is dissolved and the mixture has cooled down to room temperature. The solvent and the mainly formed $^t$Bu$_3$TAC are evaporated in vacuum (70 °C/1.3 Pa). Afterwards hexane (10 ml) is added and removed in vacuum. This procedure is repeated four or five times. Then the remaining yellowish oil is dissolved in pentane and filtered through a short column of neutral $Al_2O_3$. The filtrate is dried over sodium over night. After filtering through alumina again and slow evaporation of the solvent colorless crystals start to grow. Yield: 1.1 g ($M = 500.8$ gmol$^{-1}$, 3%) of pure **48**, m.p. $30 - 33$ °C.

| $C_{30}H_{56}N_6$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 72.14 | 11.10 | 16.35 |
| Calc: | 71.85 | 11.27 | 16.78 |

**Infrared Spectrum** (KBr; $\nu$/cm$^{-1}$)

3031m, 2963s, 2924m, 2867m, 2814m, 2801m, 2767m, 2750m, 2670m, 2601w, 1686w, 1682w, 1608w, 1478m, 1468m, 1452m, 1407m, 1393m, 1385m, 1362s, 1355s, 1305m, 1271s, 1254m, 1243m, 1218s, 1202s, 1187m, 1169s, 1155s, 1094m, 1062m, 1025m, 1005s, 984m, 971m, 938w, 911m, 900m, 869m, 837w, 795m, 783m, 756w, 707m, 644w, 524w, 505w, 502w, 498w, 495w, 476w, 469w, 440w

**$^{1}$H and $^{13}$C NMR Data**




| $^{1}$H-**NMR** (200 MHz, $CDCl_3$) | | | | $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$) |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^{1}J_{HH}$(Hz) | | $\delta$(ppm) |
| 6,7,8,9 | 7.4-7.2 | - | 4m | 147.6, 139.4, 129.5, 127.4 |
| 5 | 3.72 | - | 4s | 56.71 |
| 4 | - | - | - | 52.46 |
| 1 | 3.60 | - | 4br | 68.53 |
| 2 | 3.47 | - | 8br | 64.27 |
| 3 | 1.07 | - | 36s | 26.66 |

## 5.3 Complexes

### 5.3.1 RTATC-Complexes

SiTATCCrCl$_3$ : **49**

0.2 g ($M$ = 267.5 gmol$^{-1}$, 0.74 mmol) of SiTATC are mixed with 0.26 g of $CrCl_3 \cdot 3THF$ ($M$ = 374.7 gmol$^{-1}$, 0.69 mmol). Diethylether (20 ml) is added via vacuum transfer. After 30 min of stirring at room temperature the solvent is removed in vacuum. This procedure is repeated three times. Finally excess ligand is removed by washing with ether. Yield: 0.18 g ($M$ = 425.9 gmol$^{-1}$, 61%) of **49**, m.p. 220 − 230 °C

| $C_{14}H_{29}N_3SiCrCl_3$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 60.66 | 10.75 | 10.21 |
| Calc: | 62.86 | 10.93 | 15.71 |

**Infrared Spectrum** (KBr; $\nu$/cm$^{-1}$)

3291s, 2959s, 1611s, 1517w, 1475w, 1460w, 1440w, 1393w, 1324w, 1253m, 1175w, 1054m, 1038m, 1012m, 959w, 915w, 856s, 757w, 719w, 687m, 620m, 574m, 523s, 450m, 446m, 420w, 416w, 412w, 405w

BuTATCCrCl$_3$ : **50**

0.2 g ($M$ = 237.4 gmol$^{-1}$, 0.84 mmol) of BuTATC (**18**) are mixed with 0.32 g of $CrCl_3 \cdot 3THF$ ($M$ = 374.7 gmol$^{-1}$, 0.85 mmol). Diethylether (25 ml) is added via vacuum transfer. After 30 min of stirring at room temperature the solvent is removed in vacuum. This procedure is repeated three times. Finally excess ligand is removed by washing with ether. Yield: 0.21 g ($M$ = 395.8 gmol$^{-1}$, 63%) of **50**, m.p. 90 − 100 °C

| $C_{14}H_{27}N_3CrCl_3$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 68.81 | 11.42 | 14.21 |
| Calc: | 70.83 | 11.46 | 17.70 |

**Infrared Spectrum** (KBr; $\nu/\mathrm{cm}^{-1}$)

3279s, 2959s, 2933s, 2872m, 1601s, 1511m, 1459m, 1428m, 1385w, 1342w, 1322m, 1301w, 1203w, 1096w, 1036m, 1012m, 963m, 919m, 859s, 727m, 691m, 594m, 515s

HTATCCrCl$_3$ : **51**

0.5 g of **16** ($M = 181.3\,\mathrm{gmol}^{-1}$, 2.76 mmol) are stirred with 1.06 g of $\mathrm{CrCl_3 \cdot 3\,THF}$ ($M = 374.7\,\mathrm{gmol}^{-1}$, 2.82 mmol) in THF for 3 d. The solvent is removed in vacuum and the remaining deep purple solid washed with hexane. Yield: 0.82 g ($M = 339.6\,\mathrm{gmol}^{-1}$, 88%) of **51**, m.p. 164 − 165 °C.

| $\mathrm{C_{10}H_{19}N_3CrCl_3}$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 35.41 | 5.87 | 10.02 |
| Calc: | 35.36 | 5.64 | 12.37 |

**Infrared Spectrum** (KBr; $\nu/\mathrm{cm}^{-1}$)

3366s, 3299s, 3004s, 2950s, 2869s, 1690m, 1595s, 1467s, 1441m, 1422w, 1380w, 1372w, 1359w, 1344w, 1322m, 1285s, 1271m, 1150s, 1131w, 1107w, 1088s, 1051w, 1035w, 993w, 947m, 898w, 881w, 817w, 731w, 695w, 582m, 530m, 517m, 459w, 403m

MeTATCCrCl$_3$ : **52**

1.22 g of **17** ($M = 195.3\,\mathrm{gmol}^{-1}$, 6.24 mmol) are stirred with 2.20 g of $\mathrm{CrCl_3 \cdot 3\,THF}$ ($M = 374.7\,\mathrm{gmol}^{-1}$, 5.87 mmol) in THF for 5 d. The solvent is removed in vacuum and the remaining deep purple solid washed with THF and hexane. Yield: 1.05 g ($M = 353.7\,\mathrm{gmol}^{-1}$, 51%) of **52**, m.p. 222 − 225 °C d.

| $\mathrm{C_{11}H_{21}N_3CrCl_3}$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 36.60 | 5.84 | 8.67 |
| Calc: | 37.36 | 5.99 | 11.88 |

**Infrared Spectrum** (KBr; $\nu/\mathrm{cm}^{-1}$)

3300s, 2999s, 2959s, 2885s, 1611w, 1471m, 1438w, 1388m, 1355w, 1334w, 1297m, 1274m, 1256w, 1170m, 1151m, 1126m, 1111m, 1103w, 1064m, 1039s, 904w, 698w, 569m, 529w, 431w, 401m

MeTATCCr$(OTf)_3$ : **53**

0.4 g of **52** ($M = 353.7\,\mathrm{gmol}^{-1}$, 1.13 mmol) is stirred in pure $HSO_3CF_3$ ($\sim$ 5 ml, $\rho = 1.696$) for 2 h at room temperature. Afterwards the excess acid is removed in vacuum. The remaining light blue-green solid is washed three times with diethylether and one time with pentane. Yield: 0.76 g ($M = 694.5\,\mathrm{gmol}^{-1}$, 97%) of blue-green **53**, m.p. $215 - 215\,^{\circ}\mathrm{C}$ d.

| $C_{14}H_{21}N_3CrS_3O_9F_9$ | C | H | N | S |
|---|---|---|---|---|
| Anal. Found: | 24.09 | 3.02 | 5.84 | 14.22 |
| Calc: | 24.64 | 3.10 | 6.16 | 14.09 |

MeTATCC$rI_3$ : **54**

0.76 g of **53** ($M = 694.5\,\mathrm{gmol}^{-1}$, 1.11 mmol) are stirred with 0.5 g ($M = 140.9\,\mathrm{gmol}^{-1}$, 3.54 mmol) of NaI in $CH_2Cl_2$ for 3 d. Afterwards the dark solution is filtered. After adding of about 20 ml of diethylether the formed precipitate is filtered off again and the solvent is removed in vacuum. Yield: 0.14 g ($M = 628.0\,\mathrm{gmol}^{-1}$, 21%) of brown **54**, m.p. $219 - 229\,^{\circ}\mathrm{C}$ d.

| $C_{11}H_{21}N_3CrI_3$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 20.28 | 3.44 | 6.11 |
| Calc: | 21.45 | 3.44 | 6.82 |

**Infrared Spectrum** (KBr; $\nu/\mathrm{cm}^{-1}$)

3679m, 3479m, 3391m, 2927m, 1615m, 1524w, 1439w, 1327s, 1296s, 1271s, 1253s, 1231s, 1223s, 1188s, 1149m, 1052s, 900w, 771s, 765w, 746w, 658m, 642m, 583m, 550w, 521m, 514m, 462w, 430w, 416w

BzTATCCrCl$_3$ : **55**

1.2 g of **21** ($M = 271.4\,\mathrm{g mol^{-1}}$, 4.42 mmol) are stirred with 1.65 g of $CrCl_3 \cdot 3\,THF$ ($M = 374.7\,\mathrm{g mol^{-1}}$, 4.40 mmol) in THF for 3 d. The solvent is removed in vacuum and the remaining purple solid washed with hexane. Yield: 1.74 g ($M = 429.8\,\mathrm{g mol^{-1}}$, 92%) of **55**, m.p. $215 - 218\,^{\circ}C$.

| $C_{17}H_{25}N_3CrCl_3$ | C | H | N | Cl |
|---|---|---|---|---|
| Anal. Found: | 44.86 | 5.54 | 9.01 | 23.52 |
| Calc: | 47.51 | 5.86 | 9.78 | 24.75 |

**Infrared Spectrum** (KBr; $\nu/\mathrm{cm^{-1}}$)

3384m, 3058m, 3049m, 3005m, 2957s, 2949s, 2931s, 2883s, 2856m, 1602m, 1584m, 1494m, 1471m, 1454m, 1445w, 1436m, 1363w, 1332m, 1303m, 1275m, 1184w, 1143s, 1112s, 1093s, 1048m, 1035w, 1006w, 986w, 940w, 879w, 779m, 715s, 675m, 617w, 582m, 547w, 535w, 507m, 490m, 405s

PhTATCCrCl$_3$ : **56**

1.0 g of **20** ($M = 257.4\,\mathrm{g mol^{-1}}$, 3.88 mmol) are stirred with 1.42 g of $CrCl_3 \cdot 3\,THF$ ($M = 374.7\,\mathrm{g mol^{-1}}$, 3.80 mmol) in THF for 3 d. The solvent is removed in vacuum and the remaining purple solid washed with hexane. Yield: 1.49 g ($M = 415.7\,\mathrm{g mol^{-1}}$, 94%) of **56**, m.p. $222 - 224\,^{\circ}C$.

| $C_{16}H_{23}N_3CrCl_3$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 44.86 | 5.54 | 9.01 |
| Calc: | 46.23 | 5.57 | 10.11 |

**Infrared Spectrum** (KBr; $\nu/\mathrm{cm^{-1}}$)

3288s, 2111w, 1590s, 1573s, 1508m, 1489m, 1458m, 1382m, 1363w, 1343w, 1320m, 1302w, 1244w, 1217w, 1161w, 1113w, 1086w, 1037m, 1011m, 956w, 924m, 915m, 861s, 813w, 765m, 703m, 664m, 594m, 507m, 446s

4-$^{t}$Butyl-toluyl-TATCCrCl$_3$ : **57**

1.5 g of **22** ($M = 327.5\,\mathrm{gmol^{-1}}$, 4.57 mmol) are stirred with 1.01 g $CrCl_3 \cdot 3\,THF$ ($M = 374.7\,\mathrm{gmol^{-1}}$, 4.38 mmol) in THF for 3 d. The solvent is removed in vacuum and the remaining purple solid washed with hexane. Yield: 1.92 g ($M = 485.9\,\mathrm{gmol^{-1}}$, 90%) of **57**, m.p. $143 - 144\,^{\circ}C$.

| $C_{21}H_{33}N_3CrCl_3$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 48.29 | 6.77 | 7.42 |
| Calc: | 51.91 | 6.85 | 8.65 |

**Infrared Spectrum** (KBr; $\nu/\mathrm{cm^{-1}}$)

3293m, 3092m, 3059s, 2952s, 2894s, 2814s, 2760m, 2746m, 1888w, 1772w, 1601m, 1515m, 1482m, 1460m, 1446m, 1429m, 1411m, 1381m, 1352m, 1346m, 1322m, 1311m, 1293m, 1274s, 1244w, 1230m, 1213w, 1191m, 1176m, 1158m, 1144w, 1123m, 1111m, 1101m, 1080m, 1046m, 1012m, 979w, 963m, 948m, 920m, 907m, 894m, 855s, 813m, 785w, 752w, 740w, 709w, 683w, 660w, 610w, 606w, 597w, 577w, 549w, 535w, 478w, 462w, 441w, 420w, 411w

4-$^{t}$Butyl-toluyl-TATCCr(OTf)$_3$ : **58**

1.1 g of **57** ($M = 485.9\,\mathrm{gmol^{-1}}$, 2.26 mmol) is stirred in pure $HSO_3CF_3$ ($\sim$ 8 ml, $\rho = 1.696$) for 2 h at room temperature. Afterwards the excess acid is removed in vacuum. The remaining light blue-green solid is washed three times with diethylether and one time with pentane. Yield: 1.49 g ($M = 826.7\,\mathrm{gmol^{-1}}$, 80%) of blue-green **58**, m.p. $101 - 103\,^{\circ}C$ d.

| $C_{24}H_{33}N_3CrCl_3$ | C | H | N | S |
|---|---|---|---|---|
| Anal. Found: | 34.55 | 3.91 | 4.87 | 11.46 |
| Calc: | 34.87 | 4.02 | 5.08 | 11.64 |

**Infrared Spectrum** (KBr; $\nu/\mathrm{cm^{-1}}$)

3399m, 2967m, 2921m, 2852w, 1608m, 1514m, 1343s, 1238s, 1202s, 1006s, 889w, 860w, 840w, 814w, 769w, 727w, 710w, 637m, 573m, 557m, 512m,

428m

PhTATCCuCl$_2$ : **59**:

**20** (520 mg, 2.02 mmol) and anhydrous $CuCl_2$ (540 mg, 4.01 mmol) were stirred in $CH_2Cl_2$ (30 ml) for 12 hrs. The green solution was filtered and the solvent removed in vacuum. Yield: 430 mg (54%) of green crystalline **59**, m.p. $123 - 124$ °C.

| $C_{17}H_{23}N_3CrCl_3$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 49.51 | 5.37 | 11.11 |
| Calc: | 49.05 | 5.92 | 10.72 |

**Infrared Spectrum** (KBr; $\nu/\mathrm{cm}^{-1}$)

3436s, 3298m, 3124m, 3057m, 2957s, 2931s, 2854s, 1986w, 1696w, 1646w, 1592m, 1576w, 1500w, 1495w, 1470m, 1442m, 1407w, 1384m, 1352m, 1324w, 1313m, 1284m, 1266m, 1226w, 1204m, 1171s, 1153m, 1131s, 1104m, 1095m, 1080s, 1051w, 1038w, 1008w, 1001w, 967m, 937s, 902w, 874w, 822w, 759m, 736w, 704, 680m, 650m, 595w, 576w, 567w, 590w, 521w, 510w, 467w, 442m

HTATCFeCl$_3$: **60**

0.2 g ($M = 181.3$ gmol$^{-1}$, 1.10 mmol) of HTATC (**16**) are mixed with 0.18 g ($M = 162.2$ gmol$^{-1}$, 1.10 mmol) of anhydrous $FeCl_3$. Diethylether (20 ml) is added via vacuum transfer. After 30 minutes of stirring at room temperature the solvent is removed in vacuum. This procedure is repeated three times. Finally excess ligand is removed by washing with ether. Yield: 0.23 g ($M = 343.5$ gmol$^{-1}$, 61%) of HTATCFeCl$_3$, m.p. $95 - 96$ °C d.

| $C_{10}H_{19}N_3FeCl_3$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 31.65 | 5.62 | 10.53 |
| Calc: | 34.97 | 5.58 | 12.23 |

**Infrared Spectrum** (KBr; $\nu/\mathrm{cm}^{-1}$)

3420s, 2943s, 2867s, 1689s, 1593s, 1504w, 1456m, 1440m, 1382m, 1325s, 1305m, 1291m, 1235m, 1132w, 1111w, 1067m, 1038m, 1015w, 877m, 836w, 694w, 609w, 601w, 527w, 497w, 458m, 446m, 424w

BzTATCCuCl$_2$ : **61**:

Analogous to **59**, **21** (740 mg, $M = 271.4\,\mathrm{gmol}^{-1}$, 2.54 mmol) and anhydrous $CuCl_2$ (390 mg, $M = 134.5\,\mathrm{gmol}^{-1}$, 2.71 mmol) yielded 720 mg ($M = 405.9\,\mathrm{gmol}^{-1}$, 70%) of green crystalline **61**, m.p. 100 °C.

| $C_{17}H_{15}N_3CrCl_3$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 50.43 | 5.73 | 10.79 |
| Calc: | 50.31 | 6.21 | 10.35 |

**Infrared Spectrum** (KBr; $\nu/\mathrm{cm}^{-1}$)

3481w, 3292w, 3057w, 2999w, 2957s, 2932s, 2857s, 1812m, 1717m, 1653m, 1628m, 1598m, 1580m, 1493m, 1474m, 1468m, 1459m, 1452m, 1437m, 1407m, 1391m, 1365m, 1354m, 1326m, 1318m, 1292s, 1271m, 1242m, 1233m, 1202m, 1177m, 1157m, 1136m, 1112m, 1096m, 1088m, 1076m, 1052m, 1039m, 1012m, 997m, 959m, 934m, 920m, 911m, 898m, 890m, 876m, 842w, 833w, 812m, 780m, 752w, 717m, 671m, 613w, 597w, 578w, 548m, 514w, 495w, 490w, 459w, 410m, 409m

PhTATCFeCl$_3$ : **62**:

**20** (1.2 g, $M = 257.4\,\mathrm{gmol}^{-1}$, 4.66 mmol) and anhydrous $FeCl_3$ (0.75 g, $M = 162.2\,\mathrm{gmol}^{-1}$, 4.63 mmol) were stirred in diethylether (30 ml) for 3 d. The brown solution was filtered and the solvent removed in vacuum. Yield: 1.80 g ($M = 419.6\,\mathrm{gmol}^{-1}$, 93%) of brown crystalline **62**, m.p. 85 °C.

| $C_{17}H_{23}N_3CrCl_3$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 39.89 | 4.80 | 10.78 |
| Calc: | 45.80 | 5.53 | 10.01 |

**Infrared Spectrum** (KBr; $\nu/\mathrm{cm}^{-1}$)

3336m, 3059m, 3029m, 2941s, 2866s, 2836s, 1685m, 1650m, 1629m, 1595s, 1575m, 1510w, 1488m, 1472w, 1441s, 1383m, 1352w, 1325s, 1285w, 1248m, 1227m, 1208m, 1128w, 1038w, 942w, 857m, 759m, 701m, 595s, 523s, 510s, 461m

[(BzTATC)Zn(Et)][$BF_4$] : **63**

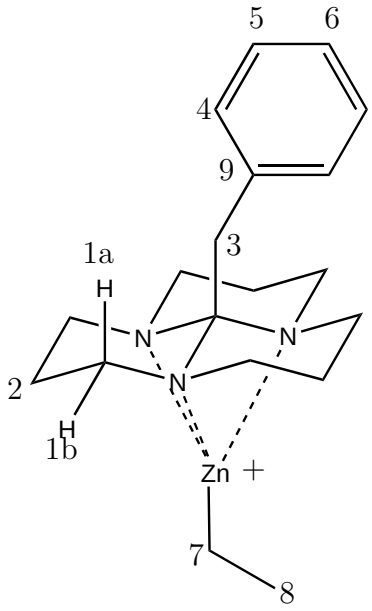
In a solution of 0.59 g of diethylzinc ($M = 123.5\ \mathrm{gmol}^{-1}$, 0.81 mmol) in hexane a solution 0.22 g of BzTATC ($M = 271.4\ \mathrm{gmol}^{-1}$, 0.81 mmol) and 0.17 g of N,N-dimethylaniliniumtetrafluoroborat ($M = 209.0\ \mathrm{gmol}^{-1}$, 0.81 mmol) in diethylether (20 ml) were added at 0 °C. After stirring for 15 min all volatile compounds are removed in vacuum. The oily product is washed three times with hexane resulting in 0.33 g ($M = 452.7\ \mathrm{gmol}^{-1}$, 89.6%) of pure white crystalline **63**, m.p.: 152 °C

| $C_{19}H_{30}N_3BF_4Zn$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 49.70 | 6.66 | 9.06 |
| Calc: | 50.41 | 6.68 | 9.28 |

**Infrared Spectrum** (KBr; $\nu/\mathrm{cm}^{-1}$1)

3589w, 3472w, 3342m, 3187w, 3104w, 3087w, 3062w, 3045w, 3030w, 2007w, 2935m, 2925m, 2864m, 2829s, 1578s, 1496m, 1485m, 1466m, 1455m, 1441m, 1429m, 1389m, 1379m, 1357m, 1333m, 1327m, 1294m, 1284m, 1273m, 1254w, 1230m, 1214m, 1201m, 1184m, 1177m, 1163m, 1144s, 1075s, 1056s, 1027s, 1003s, 998s, 964m, 931w, 898w, 860w, 827w, 768m, 711s, 670w, 647m, 547m, 536m, 520m, 494m, 478m, 462m

**$^{1}$H and $^{13}$C NMR Data**




$^{1}$H-**NMR** (200 MHz, $CDCl_3$) $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$)

| Assignment | $\delta$(ppm) | $^{1}J_{HH}$(Hz) | | $\delta$(ppm) |
|---|---|---|---|---|
| 1a | 3.3 | - | 6m | 48.7 |
| 1b | 2.9 | - | 6m | 48.80 |
| 2 | 1.96 | - | 5m | 26.3 |
| 3 | 3.63 | - | 2s | 90.9 |
| 4,5,6 | 7.15-7.6 | - | 5m | 128.9, 132.5, 128.9 |
| 7 | 0.59 | 8.0 | 2q | 1.7 |
| 8 | 1.20 | 8.0 | 3t | 11.5 |
| 9 | | | | 133.8 |

$\underline{(HTATC)_2(TATC)[(Me_3SiCH_2)_2Cr(CSiMe_3)]_2}$ : **64**

2 g of $HTATCCrCl_3$ (5.88 mmol) and 1.66 g of $(CH_3)_3SiCH_2Li$ (17.63 mmol) are thoroughly mixed. To the mixture about 30 ml of toluene are added via vacuum transfer. After warming to about $-78$ °C the mixture is stirred for

4 h. During this time it turns deep blue. The toluene is removed in vacuum and the remaining deep purple oil is distilled in vacuum. The product is soluble in pentane from which suitable crystals for a x-ray crystal analysis could be grown.

### 5.3.2 $R_3TAC$ and $R_2R'TAC$-Complexes

$\underline{(Me_3TAC)_2CuCl_2}$ : **65**

About 10 ml of a saturated solution of $CuCl_2$ in ethanol is poured under rapid stirring in about 40 ml of $Me_3TAC$. At once a bright yellow solid precipitates. The solid is filtered of and washed with pentane and stored under argon. Yield: $\sim$ 15 g, m.p. $98 - 100\,^{\circ}C$ d. For an x-ray structure analysis suitable crystals of **65** could be obtained from toluene (see fig. 27, p. 35 and A.1.11, p. 144).

Attempts to recrystallize this product from $Me_3TAC$ resulted in a reduction of the copper (see fig. 31, p. 39 and A.1.12, p. 145)

| $C_{12}H_{30}N_6CuCl_2$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 31.67 | 7.51 | 18.31 |
| Calc: | 36.69 | 7.70 | 21.39 |

**Infrared Spectrum** (KBr; $\nu/cm^{-1}$)

3520m, 3430s, 3005m, 2978m, 2967m, 2941s, 2922m, 2862m, 2805s, 2748m, 2665m, 2618m, 2532w, 2499w, 1689w, 1634w, 1486m, 1472s, 1460s, 1449s, 1428m, 1416w, 1405w, 1388m, 1276s, 1269s, 1258m, 1241m, 1228w, 1168m, 1134m, 1120s, 1111s, 1108s, 1085m, 1074m, 1060w, 1053w, 1028m, 1022m, 1016m, 996m, 991m, 935s, 931s, 892m, 861w, 833w, 830w, 809m, 785w, 686w, 608w, 564m, 546w, 515w, 500w, 492w, 488w, 484w, 480w, 472w, 461w, 450w, 443w, 435w, 431w, 427w, 423w, 419w, 416w, 408w, 404w

$[^{i}Pr_3TACCu(PPh_3)]BF_4$ : **66**

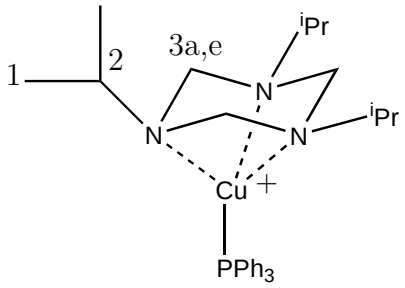
4.98 g of $[Cu(CH_3CN)_4]BF_4$ and ($M = 314.6\ gmol^{-1}$, 15.83 mmol), 4.15 g of $PPh_3$ ($M = 262.3\ gmol^{-1}$, 15.82 mmol) were suspended in about 30 ml of $CH_2Cl_2$, then a large excess of **25** ($\sim$ 6 g, $M = 174.3\ gmol^{-1}$, 28.12 mmol) was added to the suspension. After 12 h of stirring at room temperature, the solvent was removed *in vacuo* and the residue was washed with THF until the solution remained colorless. The remaining slightly yellowish solid was dried *in vacuo* to yield: 6.54 g of light yellow **66** ($M = 587.0\ gmol^{-1}$, 70%), m.p. $133 - 135\ ^{\circ}C$.

| $C_{30}H_{42}N_3CuPBF_4$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 57.21 | 6.86 | 6.53 |
| Calc: | 57.56 | 6.76 | 6.71 |

**Infrared Spectrum** (KBr; $\nu/cm^{-1}$)

3442m, 3141w, 3074w, 3056w, 3043w, 3006w, 2968s, 2931m, 2875m, 2855m, 2827w, 2764w, 2681w, 2579w, 1983w, 1899w, 1837w, 1820w, 1778w, 1684w, 1675w, 1653w, 1646w, 1635w, 1617w, 1587w, 1572w, 1521w, 1506w, 1484s, 1480s, 1466m, 1436s, 1388s, 1380w, 1369s, 1335w, 1321w, 1309w, 1297w, 1282w, 1261w, 1214s, 1168s, 1139s, 1099s, 1056s, 1036s, 1002s, 948w, 929s, 889w, 870w, 860w, 851w, 762m, 753s, 708m, 698s, 542m, 532s, 506s, 493s, 454w, 429w

**$^{1}$H and $^{13}$C NMR Data**




| $^{1}$H-**NMR** (200 MHz, $CDCl_3$) | | | $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$) | |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^{1}J_{HH}$(Hz) | | $\delta$(ppm) |
| $PPh_3$ | 7.48-7.27 | | 15m | 133.47 - 129.13 |
| 3a | 4.35 | 8.73 | 3d | 71.06 |
| 3e | 3.69 | 8.73 | 3d | 71.06 |
| 2 | 3.13 | 6.63 | 3q | 52.43 |
| 1 | 1.06 | 6.63 | 18d | 19.44 |

**$^{19}$F-NMR Data**; ($CDCl_3$)

$\delta$ = -76.14

**$^{31}$P-NMR Data**; ($CDCl_3$)

$\delta$ = 11.66

$[Bz_3TACCu(PPh_3)]BF_4$ : **67**

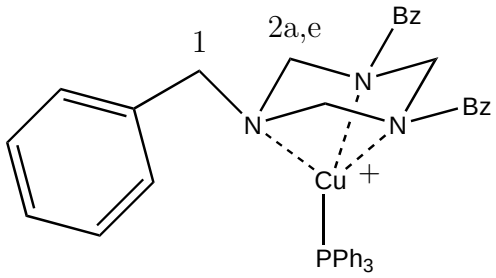
5.07 g of $[Cu(CH_3CN)_4]BF_4$ ($M$ = 314.6 gmol$^{-1}$, 16.1 mmol) and 4.2 g of $PPh_3$ ($M$ = 262.3 gmol$^{-1}$, 16.0 mmol) and 5.78 g of **26** ($M$ = 357.5 gmol$^{-1}$, 16.2 mmol) were stirred in about 30 ml of $CH_2Cl_2$. After 12 h of stirring at room temperature, the solvent was removed *in vacuo* and the residue was washed with THF until the solution remained colorless. The remaining colorless solid was dried in it vacuum to yield: 10.6 g of **67** ($M$ = 770.1 gmol$^{-1}$, 86%), m.p. 146 − 149 °C.

| $C_{42}H_{42}N_3CuPBF_4$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 64.59 | 5.52 | 5.49 |
| Calc: | 65.50 | 5.49 | 5.46 |

**Infrared Spectrum** (KBr; $\nu/cm^{-1}$)

3496w, 3141m, 3084m, 3058m, 3030m, 2988m, 2918m, 2949m, 2823m, 2786m, 1963w, 1908w, 1891w, 1820w, 1772w, 1675w, 1602w, 1586w, 1521w, 1495m, 1481m, 1471m, 1455m, 1435s, 1397w, 1355m, 1345w, 1330w, 1294w, 1285w, 1265w, 1254w, 1234w, 1209w, 1184m, 1158s, 1095s, 1081s, 1063s, 1037s, 1026s, 996m, 974m, 932m, 921m, 884w, 857w, 850w, 833w, 824w, 813w, 769w, 765w, 753s, 748s, 702s, 796s, 645w, 619w, 604w, 536m, 521m, 509m, 493m, 470w, 459w, 449w, 428w

**$^1$H and $^{13}$C NMR Data**




$^1$H-**NMR** (200 MHz, $CDCl_3$) $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$)

| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
|---|---|---|---|---|
| $CH_2Ph$, $PPh_3$ | 7.52-6.87 | | 30m | 135.03 - 128.06 |
| 2a | 4.22 | - | 3br | 75.39 |
| 2e | 3.67 | - | 3br | 75.39 |
| 1 | 3.67 | | 1s | 55.98 |

**$^{19}$F-NMR Data**; ($CDCl_3$)

$\delta$ = -74.66

**$^{31}$P-NMR Data**; ($CDCl_3$)

$\delta$ = 9.79

$\underline{d_6\text{-}[Bz_3TACCu(PPh_3)]BF_4}$ : **68**

**68** was prepared analogously to **67**.

**Infrared Spectrum** (KBr; $\nu/cm^{-1}$)

3087w, 3059m, 3031m, 3006w, 2918w, 2850m, 2233w, 2219w, 2075w, 2026w, 1963w, 1890w, 1821w, 1602w, 1586w, 1495m, 1481m, 1456s, 1435s, 1372m, 1309w, 1286w, 1262m, 1250m, 1214m, 1205m, 1184m, 1157m, 1149m, 1095s, 1084s, 1068s, 1054s, 1036s, 1027s, 1005m, 974m, 936w, 915m, 912m, 875m, 850w, 793m, 767m, 748s, 702s, 696s, 636w, 599w, 535m, 522m, 509m, 493m, 447m, 427m

$\underline{[Cy_3TACCu(PPh3)]BF_4}$ : **69**

0.47 g of $[Cu(CH_3CN)_4]BF_4$ ($M$ = 314.6 gmol$^{-1}$, 1.5 mmol) and 0.40 g of $PPh_3$ ($M$ = 262.3 gmol$^{-1}$, 1.5 mmol) and 0.50 g of **27** ($M$ = 333.6 gmol$^{-1}$, 1.5 mmol) were s tirred in about 30 ml of $CH_2Cl_2$. After 12 h of stirring at room temperature, the solvent was removed *in vacuo* and the residue was washed with THF until the solution remained colorless. The remaining colorless solid was dried *in vacuo* to yield: 1.05 g of **69** ($M$ = 746.2 gmol$^{-1}$, 94%), m.p. 133 − 135 °C.

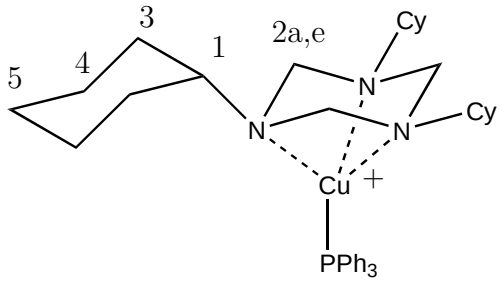
| $C_{39}H_{54}N_3CuPBF_4$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 62.05 | 7.41 | 5.39 |
| Calc: | 62.77 | 7.29 | 5.63 |

**Infrared Spectrum** (KBr; $\nu/cm^{-1}$)

3076m, 3053m, 3035w, 3008w, 2927s, 2853m, 2673w, 1886w, 1822w, 1811w,

1675w, 1653w, 1648w, 1617w, 1603w, 1587w, 1573w, 1481w, 1462w, 1449m, 1437m, 1376m, 1255w, 1197m, 1174m, 1167m, 1157m, 1127s, 1095s, 1074s, 1050s, 1038s, 997m, 947m, 927m, 916m, 892m, 756m, 749m, 746m, 705m, 696s, 537m, 528m, 520m, 505m, 490m, 450m, 447m

**$^{1}$H and $^{13}$C NMR Data**




| $^{1}$H-**NMR** (200 MHz, $CDCl_3$) | | | $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$) | |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^{1}J_{HH}$(Hz) | | $\delta$(ppm) |
| $PPh_3$ | 7.55-7.30 | | 15m | 133.29 - 129.12 |
| 2a | 4.33 | 8.6 | 3d | 71.70 |
| 2e | 3.81 | 8.6 | 3d | 71.70 |
| 1 | 2.64 | - | 3m | 60,63 |
| 3,4,5 | 1.28-1.53 | - | 30m | 29.96, 25.23 |
| | 1.28-0.99 | - | | |

**$^{19}$F-NMR Data**; ($CDCl_3$)

$\delta$ = -74.66

**$^{31}$P-NMR Data**; ($CDCl_3$)

$\delta$ = 9.79

[((S)-PhMeCH)$_3$TACCu($PPh_3$)]$BF_4$ : **70**

1.43 g of $[Cu(CH_3CN)_4]BF_4$ ($M$ = 314.6 gmol$^{-1}$, 4.54 mmol) and 1.2 g of $PPh_3$ ($M$ = 262.3 gmol$^{-1}$, 4.57 mmol) and 1.81 g of **28** ($M$ = 399.6 gmol$^{-1}$,

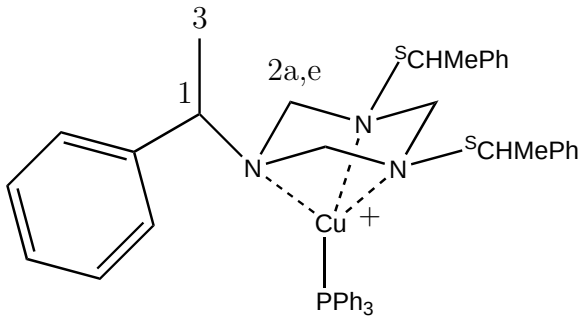
4.52 mmol) were stirred in about 30 ml of $CH_2Cl_2$. After 12 h of stirring at room temperature, the solvent was removed *in vacuo* and the residue was washed with THF until the solution remained colorless. The remaining colorless solid was dried in vacuum to yield: 3.15 g of **70** ($M = 812.2$ gmol$^{-1}$, 86%), m.p. $151 - 153$ °C.

| $C_{45}H_{48}N_3CuPBF_4$ | C | H | N |
|---|---|---|---|
| Anal. Found: | 66 06 | 5.90 | 4.66 |
| Calc: | 66.55 | 5.96 | 5.17 |

**Infrared Spectrum** (KBr; $\nu$/cm$^{-1}$)

3712w, 3450w, 3168w, 3142w, 3082w, 3061w, 3041w, 3028m, 3007w, 2973m, 2933w, 2897w, 2880m, 2829w, 2793w, 2763w, 2684w, 2125w, 1976w, 1953w, 1915w, 1896w, 1848w, 1817w, 1774w, 1692w, 1678w, 1613w, 1602w, 1585w, 1572w, 1494w, 1482w, 1471w, 1467w, 1455m, 1437m, 1435m, 1401w, 1378m, 1360w, 1345w, 1330w, 1324w, 1308w, 1284w, 1237w, 1211m, 1181m, 1161m, 1157m, 1098s, 1085s, 1060s, 1037s, 1028s, 1012m, 1000m, 988m, 978w, 971w, 964w, 955w, 938m, 924w, 918w, 788w, 783w, 775m, 762s, 755s, 751s, 706s, 700s, 656w, 565w, 536s, 521w, 508m, 494m, 447w

**$^1$H and $^{13}$C NMR Data**



| $^1$H-**NMR** (200 MHz, $CDCl_3$) | | | | $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$) |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
| CHMe*Ph*, | | | | |
| $PPh_3$ | 7.43-6.97 | | 30m | 140.2 - 127.5 |
| 2a | 4.43 | 8.6 | 3d | 66.72 |
| 2e | 8.83 | 6.4 | 3q | 66.72 |
| 1 | 3.48 | 8.6 | 3d | 59.57 |
| 3 | 1.16 | 6.4 | 9d | 18.25 |

$Bz_3$TACCuOTf : **71**:

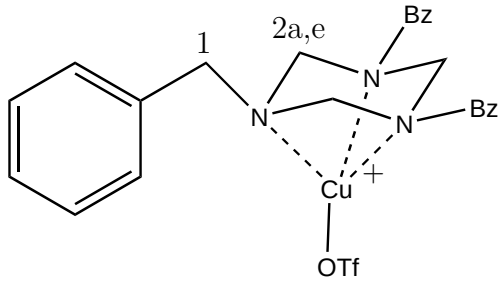
To a mixture of 0.74 g of **26** ($M = 357.5\,\mathrm{gmol^{-1}}$, 2.06 mmol) and 0.47 g of $Cu(CF_3SO_3) \cdot 0.5\,C_6H_6$ ($M = 252.7\,\mathrm{gmol^{-1}}$, 1.86 mmol) 30 ml of $CH_2Cl_2$ are added via vacuum transfer. The suspension is stirred for 8 h at room temperature. Then the solvent is removed *in vacuo* and first washed with hexane, afterwards with THF. Yield: 0.89 g ($M = 570.1\,\mathrm{gmol^{-1}}$, 84%) of light green **71**, m.p. $122 - 123\,^\circ$C.

| $C_{25}H_{27}N_3CuSO_3F_3$ | C | H | N | S |
|---|---|---|---|---|
| Anal. Found: | 52.32 | 4.79 | 6.68 | 5.41 |
| Calc: | 52.67 | 4.77 | 7.37 | 5.62 |

**Infrared Spectrum** (KBr; $\nu/\mathrm{cm^{-1}}$)

3553m, 3491w, 3087w, 3062w, 3027w, 3007w, 2964w, 2935w, 2852w, 2806w, 1966w, 1917w, 1896w, 1822w, 1773w, 1684w, 1675w, 1671w, 1663w, 1653w, 1645w, 1636w, 1622w, 1617w, 1602w, 1584w, 1576w, 1569w, 1565w, 1558w, 1554w, 1539w, 1496m, 1469m, 1456m, 1362m, 1357m, 1346m, 1338m, 1287s, 1264s, 1224m, 1199m, 1153s, 1140s, 1100m, 1081m, 1074m, 1049m, 1032s, 1002m, 997m, 972m, 927m, 915m, 768m, 756s, 705s, 655m, 637s, 620m, 606m, 572m, 550m, 517m, 454m, 451m, 447m, 443m, 436m, 432m, 428m

**$^1$H and $^{13}$C NMR Data**




| $^1$H-**NMR** (200 MHz, $CDCl_3$) | | | $^{13}$C-**NMR** (50.29 MHz, $CDCl_3$) | |
|---|---|---|---|---|
| Assignment | $\delta$(ppm) | $^1J_{HH}$(Hz) | | $\delta$(ppm) |
| $CH_2Ph$, | 7.34-7.24 | - | 15m | 131.65-129.17 |
| 2a | 4.99 | 9.0 | 3d | 74.2 |
| 1 | 4.31 | - | 6s | 59.6 |
| 2e | 2.56 | 9.0 | 3d | 74.2 |

$Me_2$OctTACCr$Cl_3$: **72**

1.5 g ($M$ = 227.4 gmol$^{-1}$, 6.59 mmol) of $Me_2$OctTAC are mixed with 2.4 g of $CrCl_3 \cdot 3\,THF$ ($M$ = 374.7 gmol$^{-1}$, 6.40 mmol). Diethylether (20 ml) is added via vacuum transfer. After 30 minute of stirring at room temperature the solvent is removed in vacuum. This procedure is repeated three times. Finally excess ligand is removed by washing with ether. Yield: 2.08 g ($M$ = 385.8 gmol$^{-1}$, 84%) of dark purple **72**, m.p. 187 °C

| $C_{13}H_{29}N_3CrCl_3$ | C | H | N | Cl |
|---|---|---|---|---|
| Anal. Found: | 41.29 | 7.74 | 10.67 | 25.52 |
| Calc: | 40.48 | 7.58 | 10.89 | 27.57 |

**Infrared Spectrum** (KBr; $\nu$/cm$^{-1}$)

2956s, 2927m, 2855s, 1687s, 1642s, 1469m, 1418s, 1378s, 1321s, 1281s, 1257m,

1236s, 1168m, 1116w, 1083w. 1006w. 925w, 724s, 543s, 539s, 535s, 531s, 512w, 420m

$Me_2BzTACCrCl_3$: **73**

1.0 g ($M$ = 205.3 gmol$^{-1}$, 4.87 mmol) of $Me_2BzTAC$ are mixed with 1.8 g of $CrCl_3 \cdot 3\,THF$ ($M$ = 374.7 gmol$^{-1}$, 4.80 mmol). Diethylether (20 ml) is added via vacuum transfer. After 30 min of stirring at room temperature the solvent is removed in vacuum. This procedure is repeated three times. Finally excess ligand is removed by washing with ether. Yield: 1.20 g ($M$ = 363.7 gmol$^{-1}$, 69%) of purple **73**, m.p. 244 - 246 °C d.

| $C_{12}H_{19}N_3CrCl_3$ | C | H | N | Cl |
|---|---|---|---|---|
| Anal. Found: | 38.79 | 5.67 | 10.85 | 28.66 |
| Calc: | 39.63 | 5.27 | 11.55 | 29.25 |

**Infrared Spectrum** (KBr; $\nu$/cm$^{-1}$)

3106m,3086m, 3061m, 3029s, 3005s, 2980s, 2929s, 2876m, 2795m, 1685s, 1640s, 1584s, 1496s, 1480s, 1465w, 1453m, 1424m, 1384s, 1366s, 1341m, 1304m, 1278w, 1259w, 1205m, 1186m, 1164w, 1139m, 1118w, 1103w, 1070m, 1028m, 1009w, 971m, 962m, 944w, 924w, 897m, 892m, 888m, 884m, 769m, 708m, 660m, 558m, 512s, 470m, 422m, 413m

$Et_2(EtCN)TACCrCl_3$: **74**

2.2 g ($M$ = 196.3 gmol$^{-1}$, 11.20 mmol) of $Et_2EtCNTAC$ are mixed with 4.0 g of $CrCl_3 \cdot 3\,THF$ ($M$ = 374.7 gmol$^{-1}$, 10.67 mmol). THF (40 ml) is added via vacuum transfer. After 1 h of stirring at room temperature the solvent is removed in vacuum. This procedure is repeated two times. Finally excess ligand is removed by washing with ether. Yield: 1.93 g ($M$ = 354.6 gmol$^{-1}$, 51%) of dark purple **74**, m.p. 246 − 248 °C d.

| $C_{10}H_{20}N_4CrCl_3$ | C | H | N | Cl |
|---|---|---|---|---|
| Anal. Found: | 33.95 | 5.98 | 15.03 | 26.41 |
| Calc: | 33.87 | 5.68 | 15.80 | 29.99 |

**Infrared Spectrum** (KBr; $\nu/\mathrm{cm}^{-1}$)

3390s, 2983s, 2953s, 2887s, 2254m, 1639s, 1486s, 1462m, 1414m, 1391s, 1377s, 1348s, 1331s, 1323s, 1303s, 1292s, 1270s, 1245s, 1202m, 1170s, 1141s, 1121w, 1097m, 1086m, 1020s, 1006s, 983s, 964m, 924w, 793m, 763m, 602m, 547m, 531w, 516m, 508m, 504m, 431m, 423m

# A X-ray data

## A.1 Parameters

Crystal and Intensity Data Collection for:

### A.1.1 PhTATC 20

| | | | | | | |
|---|---|---|---|---|---|---|
| Identification code | PhTATC | | | | | |
| Empirical formula | $C_{16}H_{23}N_3$ | | | | | |
| Formula weight | 257.37 | | | | | |
| Temperature | 293(2) K | | | | | |
| Wavelength | 0.71069 Å | | | | | |
| Crystal system | monoclinic | | | | | |
| Space group | P $2_1$ | | | | | |
| Unit cell dimensions | a = | 14.116(4) | Å | alpha | = | 90.00(2) ° |
| | b = | 7.7234(13) | Å | beta | = | 96.64(2) ° |
| | c = | 19.599(4) | Å | gamma | = | 90.00(2) ° |
| Volume | 2122.4(8) $Å^3$ | | | | | |
| Z | 6 | | | | | |
| Density (calculated) | 1.208 $Mg/m^3$ | | | | | |
| Absorption coefficient | 0.073 $mm^{-1}$ | | | | | |
| F(000) | 840 | | | | | |
| Crystal size | 0.7 x 0.45 x 1.1 mm | | | | | |
| Theta range for data collection | 1.05 ° to 23.46 ° | | | | | |
| Index ranges | 0 <= h <= 15, 0 <= k <= 8, -21 <= l <= 21 | | | | | |
| Reflections collected | 3260 | | | | | |
| Independent reflections | 3117 [R(int) = 0.0185] | | | | | |

| | |
|---|---|
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3112 / 0 / 513 |
| Goodness-of-fit on $F^2$ | 1.034 |
| Final R indices [$I > 2\sigma(I)$] | R1 = 0.0341, wR2 = 0.0851 |
| R indices (all data) | R1 = 0.0344, wR2 = 0.0888 |
| Absolute structure parameter | 0(2) |
| Largest diff. peak and hole | 0.105 eÅ$^{-3}$ and -0155 eÅ$^{-3}$ |

### A.1.2 (PhTATC)(HCl)

| | |
|---|---|
| Identification code | PhTATC · HCl |
| Empirical formula | $C_{16}H_{24}ClN_3$ |
| Formula weight | 293.83 |
| Temperature | 163(2) K |
| Wavelength | 0.71069 Å |
| Crystal system | trigonal |
| Space group | R $\bar{3}$ (No.148) |
| Unit cell dimensions | a = 15.549(4) Å alpha = 113.66(2) ° |
| | b = 15.549(3) Å beta = 113.66(2) ° |
| | c = 15.549(4) Å gamma = 113.66(2) ° |
| Volume | 2340.4(9) Å$^3$ |
| Z | 6 |
| Density (calculated) | 1.251 Mg/m$^3$ |
| Absorption coefficient | 0.240 mm$^{-1}$ |
| F(000) | 948 |
| Crystal size | 0.8 x 0.8 x 0.5 mm |
| Theta range for data collection | 1.56 ° to 24.93 ° |

| | |
|---|---|
| Index ranges | -18 <= h <= 12, -8 <= k <= 11, -11 <= l <= 15 |
| Reflections collected | 1848 |
| Independent reflections | 1287 [R(int) = 0.0192] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 1256 / 0 / 185 |
| Goodness-of-fit on $F^2$ | 1.079 |
| Final R indices [$I < 2\sigma(I)$] | R1 = 0.0637, wR2 = 0.1765 |
| R indices (all data) | R1 = 0.0829, wR2 = 0.2423 |
| Largest diff. peak and hole | 0.706 e$Å^{-3}$ and -0.744 e$Å^{-3}$ |

### A.1.3 [PhTATCH]$^+$[TFPB]$^-$

| | |
|---|---|
| Identification code | PhTATCTFPB |
| Empirical formula | $C_{48}H_{36}BF_{24}N_3$ |
| Formula weight | 1121.61 |
| Temperature | 180(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | triclinic |
| Space group | P $\bar{1}$ |
| Unit cell dimensions | a = 12.244(3) Å alpha = 110.28(2) ° |
| | b = 12.882(3) Å beta = 94.82(2) ° |
| | c = 16.511(4) Å gamma = 103.35(2) ° |
| Volume | 2338.1(11) $Å^3$ |
| Z | 2 |
| Density (calculated) | 1.593 $Mg/m^3$ |
| Absorption coefficient | 0.160 $mm^{-1}$ |
| F(000) | 1132 |

| | |
|---|---|
| Crystal size | 0.76 x 0.76 x 0.38 mm |
| Theta range for data collection | 1.99 ° to 25.27 ° |
| Index ranges | -14 <= h <= 14, -15 <= k <= 14, 0 <= l <= 19 |
| Reflections collected | 18188 |
| Independent reflections | 7810 [R(int) = 0.0617] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 7780 / 0 / 718 |
| Goodness-of-fit on $F^2$ | 1.101 |
| Final R indices [$I > 2\sigma(I)$] | R1 = 0.0735, wR2 = 0.2018 |
| R indices (all data) | R1 = 0.0923, wR2 = 0.2299 |
| Extinction coefficient | 0.023(3) |
| Largest diff. peak and hole | 0.766 eÅ$^{-3}$ and -0.506 eÅ$^{-3}$ |

### A.1.4 BzTATC 21

| | |
|---|---|
| Identification code | BzTATC |
| Empirical formula | $C_{17}H_{25}N_3$ |
| Formula weight | 271.40 |
| Temperature | 293(2) K |
| Wavelength | 0.71069 Å |
| Crystal system | monoclinic |
| Space group | P $2_1$/a (No.14) |
| Unit cell dimensions | a = 7.996(2) Å alpha = 90.000(13) ° |
| | b = 17.708(2) Å beta = 104.92(2) ° |
| | c = 11.027(3) Å gamma = 90.00(2) ° |
| Volume | 1508.8(6) Å$^3$ |
| Z | 4 |

| | |
|---|---|
| Density (calculated) | 1.195 $Mg/m^3$ |
| Absorption coefficient | 0.072 $mm^{-1}$ |
| F(000) | 592 |
| Crystal size | 0.5 x 0.25 x 0.7 mm |
| Theta range for data collection | 1.91 ° to 25.94 ° |
| Index ranges | 0 <= h <= 9, 0 <= k <= 21, -13 <= l <= 13 |
| Reflections collected | 3333 |
| Independent reflections | 1924 [R(int) = 0.0100] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 1903 / 0 / 181 |
| Goodness-of-fit on $F^2$ | 1.094 |
| Final R indices [$I < 2\sigma(I)$] | R1 = 0.0483, wR2 = 0.1259 |
| R indices (all data) | R1 = 0.0500, wR2 = 0.1346 |
| Largest diff. peak and hole | 0.176 $eÅ^{-3}$ and -0.160 $eÅ^{-3}$ |

### A.1.5 [TATC][$Fe_2Cl_6O$](THF)

| | | | | | | |
|---|---|---|---|---|---|---|
| Identification code | [TATC][Fe2Cl6O] | | | | | |
| Empirical formula | $C_{11}H_{9.50}C_{l3}FeN_4O$ | | | | | |
| Formula weight | 375.93 | | | | | |
| Temperature | 163(2) K | | | | | |
| Wavelength | 0.71069 Å | | | | | |
| Crystal system | orthorhrombic | | | | | |
| Space group | P n m a (No.62) | | | | | |
| Unit cell dimensions | a = | 20.769(3) | Å | alpha | = | 90.00(2) ° |
| | b = | 12.148(4) | Å | beta | = | 90.00(2) ° |
| | c = | 13.588(3) | Å | gamma | = | 90.00(2) ° |

| | |
|---|---|
| Volume | 3428.1(14) $Å^3$ |
| Z | 8 |
| Density (calculated) | 1.457 $Mg/m^3$ |
| Absorption coefficient | 1.346 $mm^{-1}$ |
| F(000) | 1508 |
| Crystal size | 0.75 x 0.55 x 0.6 mm |
| Theta range for data collection | 1.79 ° to 24.96 ° |
| Index ranges | 0 <= h <= 24, 0 <= k <= 14, 0 <= l <= 15 |
| Reflections collected | 3409 |
| Independent reflections | 1425 [R(int) = 0.0000] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 1400 / 0 / 193 |
| Goodness-of-fit on $F^2$ | 1.113 |
| Final R indices [$I < 2\sigma(I)$] | R1 = 0.0747, wR2 = 0.1814 |
| R indices (all data) | R1 = 0.0808, wR2 = 0.2044 |
| Largest diff. peak and hole | 0.608 $eÅ^{-3}$ and -0.414 $eÅ^{-3}$ |

### A.1.6 $[\mathbf{TATC}]_2[\mathbf{Fe_2Cl_6}](\mathbf{Et_2O})$

| | |
|---|---|
| Identification code | [C10H18N3]2[Fe2Cl6](Et2O) |
| Empirical formula | $C_{24}H_{36}C_{l6}Fe_2N_6O$ |
| Formula weight | 748.99 |
| Temperature | 163(2) K |
| Wavelength | 0.71069 Å |
| Crystal system | monoclinic |
| Space group | C 2/c (No.15) |
| Unit cell dimensions | a = 20.614(6) Å alpha = 90.00(3) ° |

| | |
|---|---|
| | b = 11.371(3) Å beta = 99.60(3) ° |
| | c = 14.487(6) Å gamma = 90.00(2) ° |
| Volume | 3348(2) $Å^3$ |
| Z | 4 |
| Density (calculated) | 1.486 $Mg/m^3$ |
| Absorption coefficient | 1.348 $mm^{-1}$ |
| F(000) | 1536 |
| Crystal size | 0.2 x 0.4 x 0.6 mm |
| Theta range for data collection | 2.00 ° to 23.97 ° |
| Index ranges | -23 <= h <= 23, 0 <= k <= 12, 0 <= l <= 16 |
| Reflections collected | 3364 |
| Independent reflections | 1978 [R(int) = 0.0510] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 1937 / 6 / 167 |
| Goodness-of-fit on $F^2$ | 1.108 |
| Final R indices [I $< 2\sigma$(I)] | R1 = 0.1064, wR2 = 0.2799 |
| R indices (all data) | R1 = 0.1144, wR2 = 0.3186 |
| Largest diff. peak and hole | 2.521 $eÅ^{-3}$ and -1.038 $eÅ^{-3}$ |

### A.1.7 [PhTATC][$FeCl_3$-O-$FeCl_3$]

| | |
|---|---|
| Identification code | [PhTATC][FeCl3-O-FeCl3] |
| Empirical formula | $C_{32}H_{48}C_{l6}Fe_2N_6O$ |
| Formula weight | 857.16 |
| Temperature | 166(2) K |
| Wavelength | 0.71069 Å |
| Crystal system | monoclinic |

| | | | | | | |
|---|---|---|---|---|---|---|
| Space group | P $2_1/c$ | | | | | |
| Unit cell dimensions | a = | 14.910(6) | Å | alpha | = | 90.00(4) ° |
| | b = | 16.747(93) | Å | beta | = | 100.12(4) ° |
| | c = | 15.512(7) | Å | gamma | = | 90.00(4) ° |
| Volume | 3813.2(213) $Å^3$ | | | | | |
| Z | 4 | | | | | |
| Density (calculated) | 1.490 $Mg/m^3$ | | | | | |
| Absorption coefficient | 1.194 $mm^{-1}$ | | | | | |
| F(000) | 1768 | | | | | |
| Crystal size | 1.0 x 0.7 x 0.4 mm | | | | | |
| Theta range for data collection | 1.39 ° to 22.96 ° | | | | | |
| Index ranges | -16 <= h <= 16, 0 <= k <= 18, 0 <= l <= 16 | | | | | |
| Reflections collected | 5989 | | | | | |
| Independent reflections | 4406 [R(int) = 0.0942] | | | | | |
| Absorption correction | Empirical (DIFABS) | | | | | |
| Refinement method | Full-matrix least-squares on $F^2$ | | | | | |
| Data / restraints / parameters | 4392 / 0 / 428 | | | | | |
| Goodness-of-fit on $F^2$ | 1.027 | | | | | |
| Final R indices [I < $2\sigma$(I)] | R1 = 0.0412, wR2 = 0.1067 | | | | | |
| R indices (all data) | R1 = 0.0417, wR2 = 0.1101 | | | | | |
| Largest diff. peak and hole | 0.651 e$Å^{-3}$ and -0.389 e$Å^{-3}$ | | | | | |

### A.1.8 (PhTATC)$CuCl_2$

| | |
|---|---|
| Identification code | PhTATCCuCl2 |
| Empirical formula | $C_{16}H_{23}C_{l2}CuN_3$ |
| Formula weight | 391.82 |

| | |
|---|---|
| Temperature | 163(2) K |
| Wavelength | 0.71069 Å |
| Crystal system | monoclinic |
| Space group | P $2_1$/c (No.14) |
| Unit cell dimensions | a = 8.896(4) Å alpha = 90.00(3) ° |
| | b = 12.082(4) Å beta = 103.03(4) ° |
| | c = 16.087(8) Å gamma = 90.00(4) ° |
| Volume | 1684.5(13) $Å^3$ |
| Z | 4 |
| Density (calculated) | 1.545 $Mg/m^3$ |
| Absorption coeffcient | 1.586 $mm^{-1}$ |
| F(000) | 812 |
| Crystal size | 0.35 x 0.45 x 1.1 mm |
| Theta range for data collection | 2.13 ° to 23.97 ° |
| Index ranges | -8 <= h <= 8, 0 <= k <= 13, 0 <= l <= 18 |
| Reflections collected | 2638 |
| Independent reflections | 2120 [R(int) = 0.0647] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 2106 / 0 / 207 |
| Goodness-of-fit on $F^2$ | 1.056 |
| Final R indices [$I < 2\sigma(I)$] | R1 = 0.0276, wR2 = 0.0714 |
| R indices (all data) | R1 = 0.0284, wR2 = 0.0759 |
| Largest diff. peak and hole | 0.319 $eÅ^{-3}$ and -0.260 $eÅ^{-3}$ |

### A.1.9 $[(^{i}Pr_3TAC)Cu(PPh_3)]BF_4$

| | |
|---|---|
| Identification code | iPr3TACCuPPh3BF4 |

| | |
|---|---|
| Empirical formula | $C_{30}H_{42}BCuF_4N_3P$ |
| Formula weight | 626.00 |
| Temperature | 190(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | orthorhombic |
| Space group | P n a $2_1$ (no.33) |
| Unit cell dimensions | a = 20.359(2) Å alpha = 90° |
| | b = 10.198(2) Å beta = 90° |
| | c = 30.121(2) Å gamma = 90° |
| Volume | 6253.9(11) $Å^3$ |
| Z | 8 |
| Density (calculated) | 1.330 $Mg/m^3$ |
| Absorption coefficient | 0.783 $mm^{-1}$ |
| F(000) | 2624 |
| Crystal size | 0.46 x 0.34 x 0.23 mm |
| Theta range for data collection | 2.00 ° to 25.01 ° |
| Index ranges | 0 <= h <= 24, 0 <= k <= 12, -35 <= l <= 0 |
| Reflections collected | 6154 |
| Independent reflections | 5625 [R(int) = 0.0000] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 5608 / 1 / 721 |
| Goodness-of-fit on $F^2$ | 1.025 |
| Final R indices [$I > 2\sigma(I)$] | R1 = 0.0391, wR2 = 0.0890 |
| R indices (all data) | R1 = 0.0603, wR2 = 0.1011 |
| Absolute structure parameter | -0.004(14) |
| Largest diff. peak and hole | 0.447 $eÅ^{-3}$ and -0.346 $eÅ^{-3}$ |

### A.1.10 $[(\mathbf{Bz_3TAC})\mathbf{CuPPh_3}][\mathbf{BF_4}] \cdot \mathbf{0.5\,Tol}$

| | |
|---|---|
| Identification code | Bz3TACCuPPh3BF4 |
| Empirical formula | $C_{45.50}H_{42}BCuF_4N_3P$ |
| Formula weight | 812.15 |
| Temperature | 160(2) K |
| Wavelength | 0.71069 Å |
| Crystal system | triclinic |
| Space group | P $\bar{1}$ |
| Unit cell dimensions | a = 8.904(2) Å alpha = 84.87(2) °<br>b = 11.743(2) Å beta = 83.83(2) °<br>c = 20.452(4) Å gamma = 75.08(2) ° |
| Volume | 2050.1(7) $Å^3$ |
| Z | 2 |
| Density (calculated) | 1.316 $Mg/m^3$ |
| Absorption coefficient | 0.614 $mm^{-1}$ |
| F(000) | 842 |
| Crystal size | 0.2 x 0.25 x 0.8 mm |
| Theta range for data collection | 1.00 ° to 25.95 ° |
| Index ranges | 0 <= h <= 10, -13 <= k <= 14, -25 <= l <= 25 |
| Reflections collected | 8544 |
| Independent reflections | 7995 [R(int) = 0.0215] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 7978 / 0 / 538 |
| Goodness-of-fit on $F^2$ | 1.026 |
| Final R indices [I > $4\sigma$(I)] | R1 = 0.0478, wR2 = 0.1214 |
| R indices (all data) | R1 = 0.0762, wR2 = 0.1420 |
| Largest diff. peak and hole | 1.727 $eÅ^{-3}$ and -0.474 $eÅ^{-3}$ |

### A.1.11 $(Me_3TAC)_2CuCl_2 \cdot (C_7H_8)_{0.5}$

| | |
|---|---|
| Identification code | DiMe3TACCuCl2 |
| Empirical formula | $C_{15.50}H_{30}C_{l2}CuN_6$ |
| Formula weight | 434.90 |
| Temperature | 180(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | monoclinic |
| Space group | P $2_1$/c |
| Unit cell dimensions | a = 8.7484(10) Å alpha = 90 °<br>b = 13.315(2) Å beta = 95.538(10) °<br>c = 18.634(2) Å gamma = 90 ° |
| Volume | 2160.5(4) $Å^3$ |
| Z | 4 |
| Density (calculated) | 1.337 $Mg/m^3$ |
| Absorption coefficient | 1.247 $mm^{-1}$ |
| F(000) | 912 |
| Crystal size | 10.15 x 0.15 x 0.08 mm |
| Theta range for data collection | 1.88 ° to 24.46 ° |
| Index ranges | -10 <= h <= 10, 0 <= k <= 15, 0 <= l <= 21 |
| Reflections collected | 14033 |
| Independent reflections | 3519 [R(int) = 0.0422] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3511 / 0 / 236 |
| Goodness-of-fit on $F^2$ | 0.918 |
| Final R indices [I > $2\sigma$(I)] | R1 = 0.0520, wR2 = 0.1202 |
| R indices (all data) | R1 = 0.0827, wR2 = 0.1384 |
| Extinction coefficient | 0.0073(9) |

| | |
|---|---|
| Largest diff. peak and hole | 0.462 eÅ$^{-3}$ and -0.734 eÅ$^{-3}$ |

### A.1.12 $(Me_3TAC)_6(CuCl_3)_2(Cu_2Cl_4)$

| | |
|---|---|
| Identification code | Me3TAC6CuClx |
| Empirical formula | $C_{36}H_{84}Cl_{10}Cu_4N_{18}$ |
| Formula weight | 1377.91 |
| Temperature | 170(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | orthorhombic |
| Space group | P n a $2_1$ (no.33) |
| Unit cell dimensions | a = 43.680(10) Å alpha = 90° |
| | b = 16.730(4) Å beta = 90° |
| | c = 8.335(3) Å gamma = 90° |
| Volume | 6091(3) Å$^3$ |
| Z | 4 |
| Density (calculated) | 1.503 Mg/m$^3$ |
| Absorption coefficient | 1.829 mm$^{-1}$ |
| F(000) | 2848 |
| Crystal size | 0.38 x 0.11 x 0.08 mm |
| Theta range for data collection | 2.23 ° to 26.13 ° |
| Index ranges | -53 <= h <= 53, -20 <= k <= 20, -10 <= l <= 10 |
| Reflections collected | 71501 |
| Independent reflections | 12039 [R(int) = 0.1584] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 12039 / 1 / 613 |
| Goodness-of-fit on $F^2$ | 1.027 |

| | |
|---|---|
| Final R indices [I > 2$\sigma$(I)] | R1 = 0.0649, wR2 = 0.1503 |
| R indices (all data) | R1 = 0.1123, wR2 = 0.1750 |
| Absolute structure parameter | -0.02(2) |
| Largest diff. peak and hole | 0.545 eÅ$^{-3}$ and -0.583 eÅ$^{-3}$ |

### A.1.13 ($^{t}$Bu$_2$TACCH$_2$)-m$C_6H_4$-(CH$_2$TAC$^{t}$Bu$_2$)

| | |
|---|---|
| Identification code | tBumXTAC |
| Empirical formula | $C_{30}H_{56}N_6$ |
| Formula weight | 500.81 |
| Temperature | 180(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | monoclinic |
| Space group | P $2_1$/c |
| Unit cell dimensions | a = 10.919(4) Å alpha = 102.29(4) ° |
| | b = 11.439(4) Å beta = 92.26(4) ° |
| | c = 14.026(5) Å gamma = 113.26(4) ° |
| Volume | 1557.8(9) Å$^3$ |
| Z | 2 |
| Density (calculated) | 1.068 Mg/m$^3$ |
| Absorption coefficient | 0.064 mm$^{-1}$ |
| F(000) | 556 |
| Crystal size | 0.50 x 0.40 x 0.20 mm |
| Theta range for data collection | 2.00 ° to 25.32 ° |
| Index ranges | -12 <= h <= 12, -13 <= k <= 13, -16 <= l <= 15 |
| Reflections collected | 9930 |
| Independent reflections | 8674 [R(int) = 0.2900] |

| | |
|---|---|
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 8674 / 3 / 650 |
| Goodness-of-fit on $F^2$ | 0.885 |
| Final R indices [$I > 2\sigma(I)$] | R1 = 0.1063, wR2 = 0.2602 |
| R indices (all data) | R1 = 0.2528, wR2 = 0.3243 |
| Absolute structure parameter | 4(10) |
| Extinction coefficient | 0.026(4) |
| Largest diff. peak and hole | 0.456 eÅ$^{-3}$ and -0.301 eÅ$^{-3}$ |

### A.1.14 $(\mathbf{HTATC})_2(\mathbf{TATC})[(\mathbf{Me_3SiCH_2})_2\mathbf{Cr}(\mathbf{CSiMe_3})]_2$

| | | | | | | |
|---|---|---|---|---|---|---|
| Identification code | TMSCr | | | | | |
| Empirical formula | $C_{27}H_{58}CrN_{4.50}Si_3$ | | | | | |
| Formula weight | 582.05 | | | | | |
| Temperature | 160(2) K | | | | | |
| Wavelength | 0.71069 Å | | | | | |
| Crystal system | monoclinic | | | | | |
| Space group | P $2_1$/n (No.13) | | | | | |
| Unit cell dimensions | a = | 12.033(4) | Å | alpha | = | 90 ° |
| | b = | 13.26(3) | Å | beta | = | 96.98(3) ° |
| | c = | 21.952(7) | Å | gamma | = | 90 ° |
| Volume | 3476(7) Å$^3$ | | | | | |
| Z | 4 | | | | | |
| Density (calculated) | 1.112 Mg/m$^3$ | | | | | |
| Absorption coefficient | 0.444 mm$^{-1}$ | | | | | |
| F(000) | 1270 | | | | | |
| Crystal size | 0.9 x 0.9 x 0.8 mm | | | | | |

| | |
|---|---|
| Theta range for data collection | 1.54 ° to 23.48 ° |
| Index ranges | 0 <= h <= 13, 0 <= k <= 14, -24 <= l <= 24 |
| Reflections collected | 5406 |
| Independent reflections | 5128 [R(int) = 0.0256] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 5093 / 0 / 335 |
| Goodness-of-fit on $F^2$ | 1.033 |
| Final R indices [$I > 2\sigma(I)$] | R1 = 0.0746, wR2 = 0.1850 |
| R indices (all data) | R1 = 0.1089, wR2 = 0.2238 |
| Largest diff. peak and hole | 1.021 eÅ$^{-3}$ and -0 .833 eÅ$^{-3}$ |

## A.2 Atomic coordinates

Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2 \cdot 10^3$). U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

### A.2.1 PhTATC

| Atom | x | y | z | U(eq) | Atom | x | y | z | U(eq) |
|---|---|---|---|---|---|---|---|---|---|
| N(1) | 3658(1) | -886(4) | 1758(1) | 40(1) | C(24) | 4031(2) | 2070(6) | 4426(2) | 75(1) |
| N(2) | 4471(1) | 1429 | 2396(1) | 37(1) | C(25) | 4261(2) | 1339(6) | 5138(2) | 81(1) |
| N(3) | 5006(1) | 512(4) | 1328(1) | 39(1) | C(26) | 3351(2) | 1079(5) | 5457(2) | 69(1) |
| C(1) | 4155(2) | 769(4) | 1702(1) | 34(1) | C(27) | 1777(2) | 1897(5) | 4413(1) | 45(1) |
| C(2) | 4134(2) | -2166(5) | 2237(2) | 55(1) | C(28) | 1002(2) | 1511(5) | 4764(2) | 54(1) |
| C(3) | 4360(2) | -1358(5) | 2938(2) | 60(1) | C(29) | 293(2) | 404(5) | 4486(2) | 69(1) |
| C(4) | 4977(2) | 184(5) | 2865(1) | 49(1) | C(30) | 336(3) | -321(6) | 3852(2) | 76(1) |
| C(5) | 5016(2) | 3036(5) | 2358(1) | 50(1) | C(31) | 1092(3) | 34(6) | 3504(2) | 76(1) |
| C(6) | 5905(2) | 2782(5) | 1999(2) | 56(1) | C(32) | 1813(2) | 1131(5) | 3778(2) | 62(1) |
| C(7) | 5625(2) | 2015(5) | 1295(1) | 50(1) | N(7) | 1305(2) | 1634(4) | 7500(1) | 45(1) |
| C(8) | 4860(2) | -415(5) | 672(1) | 50(1) | N(8) | 668(2) | -929(4) | 7970(1) | 49(1) |
| C(9) | 4285(2) | -2047(5) | 717(2) | 57(1) | N(9) | 2123(1) | 352(4) | 8528(1) | 41(1) |
| C(10) | 3411(2) | -1654(5) | 1075(2) | 53(1) | C(33) | 1172(2) | 702(5) | 8139(1) | 36(1) |
| C(11) | 3385(2) | 2056(4) | 1392(1) | 38(1) | C(34) | 1674(2) | 611(6) | 6961(1) | 62(1) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C(12) | 2644(2) | 2401(5) | 1782(1) | 47(1) | C(35) | 1042(2) | -894(7) | 6787(2) | 79(1) |
| C(13) | 1926(2) | 3550(5) | 1553(2) | 59(1) | C(36) | 1023(2) | -1971(5) | 7426(2) | 72(1) |
| C(14) | 1919(2) | 4348(5) | 929(2) | 61(1) | C(37) | 603(2) | -1948(5) | 8591(2) | 67(1) |
| C(15) | 2637(2) | 4003(5) | 528(2) | 59(1) | C(38) | 1575(2) | -2405(6) | 8971(2) | 72(1) |
| C(16) | 3368(2) | 2862(5) | 762(1) | 49(1) | C(39) | 2131(2) | -759(6) | 9134(1) | 58(1) |
| N(4) | 2771(2) | 2651(4) | 5452(1) | 47(1) | C(40) | 2760(2) | 1842(5) | 8657(2) | 58(1) |
| N(5) | 1970(2) | 4864(4) | 4758(1) | 49(1) | C(41) | 2843(2) | 2845(5) | 8012(2) | 67(1) |
| N(6) | 3381(2) | 3546(5) | 4414(1) | 55(1) | C(42) | 1861(2) | 3211(5) | 7653(2) | 62(1) |
| C(17) | 2502(2) | 3250(5) | 4744(1) | 42(1) | C(43) | 477(2) | 1860(5) | 8498(1) | 38(1) |
| C(18) | 3224(2) | 3957(6) | 5922(2) | 63(1) | C(44) | -387(2) | 2283(5) | 8115(1) | 46(1) |
| C(19) | 2585(2) | 5489(6) | 5937(2) | 70(1) | C(45) | -1040(2) | 3355(5) | 8381(2) | 54(1) |
| C(20) | 2401(2) | 6201(5) | 5224(2) | 68(1) | C(46) | -844(2) | 4037(5) | 9029(2) | 57(1) |
| C(21) | 1738(3) | 5544(6) | 4059(2) | 72(1) | C(47) | -7(2) | 3614(5) | 9418(2) | 59(1) |
| C(22) | 2620(3) | 5972(7) | 3723(2) | 87(1) | C(48) | 650(2) | 2528(5) | 9154(1) | 49(1) |
| C(23) | 3278(3) | 4447(6) | 3742(2) | 76(1) | | | | | |

### A.2.2 PhTATC· HCl

| Atom | x | y | z | U(eq) | Atom | x | y | z | U(eq) |
|---|---|---|---|---|---|---|---|---|---|
| Cl(1) | 4386(1) | 1884(1) | -3718(1) | 35(1) | C(7) | 6088(5) | 5380(5) | -2024(5) | 39(1) |
| N(1) | 6944(4) | 4221(4) | -1078(4) | 22(1) | C(8) | 6688(5) | 5972(5) | -37(5) | 39(1) |
| N(2) | 8148(4) | 5507(4) | -1355(4) | 33(1) | C(9) | 5832(5) | 4670(6) | -480(6) | 37(1) |
| N(3) | 7101(4) | 5968(4) | -741(4) | 30(1) | C(10) | 6478(5) | 4150(5) | -413(5) | 29(1) |
| C(1) | 7811(5) | 5589(5) | -608(5) | 25(1) | C(11) | 9058(5) | 6589(5) | 801(5) | 28(1) |
| C(2) | 7414(5) | 3533(5) | -1213(5) | 30(1) | C(12) | 9585(5) | 6412(5) | 1595(5) | 30(1) |
| C(3) | 7887(5) | 3634(5) | -1875(5) | 39(1) | C(13) | 10738(5) | 7416(5) | 2822(5) | 33(1) |
| C(4) | 8755(5) | 4981(5) | -1328(5) | 40(1) | C(14) | 11398(5) | 8629(6) | 3295(5) | 42(1) |
| C(5) | 7139(5) | 4906(6) | -2668(5) | 41(1) | C(15) | 10878(6) | 8818(6) | 2506(6) | 69(2) |
| C(6) | 6609(6) | 5543(6) | -2634(5) | 48(2) | C(16) | 9735(6) | 7823(6) | 1284(6) | 61(2) |

### A.2.3 $[\mathbf{PhTATCH}]^{+}[\mathbf{TFPB}]^{-}$

| Atom | x | y | z | U(eq) | Atom | x | y | z | U(eq) |
|---|---|---|---|---|---|---|---|---|---|
| B | 5083(3) | 11526(3) | 2848(2) | 29(1) | C(20) | 4369(2) | 10861(3) | 3412(2) | 29(1) |
| C(21) | 4437(3) | 9790(3) | 3392(2) | 32(1) | C(22) | 3880(3) | 9260(3) | 3908(2) | 35(1) |
| C(23) | 3901(3) | 8077(3) | 3799(3) | 47(1) | F(1) | 4805(2) | 7800(2) | 3492(2) | 75(1) |
| F(2) | 2987(3) | 7293(2) | 3256(3) | 97(1) | F(3) | 3948(3) | 7912(2) | 4550(2) | 76(1) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C(24) | 3254(3) | 9813(3) | 4483(2) | 38(1) | C(25) | 3184(3) | 10883(3) | 4530(2) | 36(1) |
| C(26) | 2485(3) | 11491(3) | 5122(2) | 46(1) | F(4) | 3039(3) | 12497(3) | 5683(2) | 97(1) |
| F(5) | 1647(3) | 11678(4) | 4694(2) | 113(1) | F(6) | 1998(5) | 10916(4) | 5558(3) | 175(3) |
| C(27) | 3728(3) | 11397(3) | 3998(2) | 32(1) | C(30) | 6229(2) | 12398(2) | 3564(2) | 28(1) |
| C(31) | 6197(3) | 13464(3) | 4174(2) | 31(1) | C(32) | 7098(3) | 14158(3) | 4861(2) | 32(1) |
| C(33) | 6981(3) | 15228(3) | 5523(2) | 45(1) | F(7) | 6400(3) | 15767(3) | 5204(2) | 113(1) |
| F(8) | 6344(5) | 15004(3) | 6078(3) | 148(2) | F(9) | 7926(2) | 15964(3) | 6003(2) | 111(1) |
| C(34) | 8099(3) | 13834(3) | 4960(2) | 35(1) | C(35) | 8145(3) | 12787(3) | 4365(2) | 32(1) |
| C(36) | 9191(3) | 12398(3) | 4475(2) | 39(1) | F(10) | 9028(3) | 11579(4) | 4777(3) | 120(2) |
| F(11) | 10078(2) | 13218(3) | 4976(3) | 122(2) | F(12) | 9524(2) | 11947(3) | 3728(2) | 89(1) |
| C(37) | 7226(3) | 12085(3) | 3692(2) | 32(1) | C(40) | 5363(2) | 10618(3) | 1970(2) | 29(1) |
| C(41) | 4582(3) | 9549(3) | 1468(2) | 31(1) | C(42) | 4780(3) | 8790(3) | 704(2) | 34(1) |
| C(43) | 3961(3) | 7621(3) | 234(2) | 40(1) | F(13) | 2941(2) | 7516(2) | 462(2) | 80(1) |
| F(14) | 4345(2) | 6815(2) | 395(2) | 82(1) | F(15) | 3760(2) | 7298(2) | -627(2) | 76(1) |
| C(44) | 5775(3) | 9071(3) | 386(2) | 37(1) | C(45) | 6564(3) | 10140(3) | 870(2) | 34(1) |
| C(46) | 7671(3) | 10429(3) | 567(2) | 43(1) | F(16) | 8302(2) | 11500(3) | 1014(2) | 93(1) |
| F(17) | 8301(2) | 9740(3) | 623(2) | 93(1) | F(18) | 7539(2) | 10325(3) | -261(2) | 68(1) |
| C(47) | 6355(3) | 10891(3) | 1633(2) | 32(1) | C(50) | 4316(2) | 12205(3) | 2471(2) | 29(1) |
| C(51) | 3129(3) | 11757(3) | 2206(2) | 32(1) | C(52) | 2466(3) | 12277(3) | 1839(2) | 34(1) |
| C(53) | 1197(3) | 11780(3) | 1584(2) | 41(1) | F(19) | 869(2) | 10630(2) | 1266(2) | 62(1) |
| F(20) | 675(2) | 12078(3) | 2266(2) | 86(1) | F(21) | 741(2) | 12064(3) | 973(2) | 94(1) |
| C(54) | 2972(3) | 13294(3) | 1732(2) | 37(1) | C(55) | 4144(3) | 13745(3) | 1971(2) | 37(1) |
| C(56) | 4696(4) | 14832(3) | 1853(3) | 52(1) | F(22) | 3992(5) | 15424(6) | 1752(7) | 92(4) |
| F(23) | 5421(7) | 15630(4) | 2616(5) | 71(2) | F(24) | 5352(16) | 14741(6) | 1292(10) | 142(7) |
| F(22A) | 4201(26) | 15574(13) | 2088(20) | 193(14) | F(23A) | 5721(8) | 15125(21) | 1966(21) | 127(11) |
| F(24A) | 4461(13) | 14569(10) | 943(7) | 92(4) | C(57) | 4808(3) | 13210(3) | 2331(2) | 32(1) |
| C(1) | 1322(3) | 3020(3) | 7862(2) | 36(1) | N(1) | 2161(2) | 3448(3) | 8553(2) | 43(1) |
| C(2) | 2881(3) | 2749(4) | 8721(3) | 57(1) | C(8) | 143(4) | 3357(4) | 9564(3) | 56(1) |
| C(9) | 1398(4) | 4023(4) | 9944(3) | 59(1) | C(10) | 2108(4) | 4422(3) | 9330(3) | 55(1) |
| C(11) | 886(3) | 3877(3) | 7603(2) | 37(1) | C(12) | -171(3) | 4094(4) | 7667(3) | 50(1) |
| C(13) | -420(4) | 4952(4) | 7421(3) | 58(1) | C(14) | 368(4) | 5591(3) | 7104(3) | 52(1) |
| C(15) | 1397(4) | 5356(4) | 7015(3) | 58(1) | C(16) | 1662(3) | 4510(3) | 7261(3) | 49(1) |

### A.2.4 BzTATC

| Atom | x | y | z | U(eq) | Atom | x | y | z | U(eq) |
|---|---|---|---|---|---|---|---|---|---|
| N(1) | 4108(2) | 708(1) | 8445(2) | 52(1) | C(8) | 6210(3) | 978(2) | 6736(3) | 75(1) |
| N(2) | 1623(2) | 1180(1) | 6929(2) | 53(1) | C(9) | 7020(3) | 866(2) | 8123(3) | 83(1) |
| N(3) | 4439(2) | 1267(1) | 6519(2) | 53(1) | C(10) | 5840(3) | 391(2) | 8688(3) | 76(1) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 3299(2) | 803(1) | 7107(2) | 43(1) | C(11) | 2965(3) | 1(1) | 6510(2) | 59(1) |
| C(2) | 4080(3) | 1379(1) | 9230(2) | 69(1) | C(12) | 2211(3) | -581(1) | 7220(2) | 53(1) |
| C(3) | 2275(3) | 1670(2) | 9022(3) | 76(1) | C(13) | 867(3) | -433(2) | 7748(3) | 74(1) |
| C(4) | 1613(3) | 1856(1) | 7684(3) | 70(1) | C(14) | 198(4) | -979(2) | 8372(3) | 84(1) |
| C(5) | 810(3) | 1354(2) | 5601(3) | 77(1) | C(15) | 834(4) | -1694(2) | 8486(3) | 79(1) |
| C(6) | 1972(4) | 1804(2) | 4981(3) | 86(1) | C(16) | 2136(4) | -1864(2) | 7947(3) | 80(1) |
| C(7) | 3678(4) | 1419(2) | 5180(2) | 77(1) | C(17) | 2837(3) | -1315(1) | 7326(2) | 66(1) |

### A.2.5 [TATC][$Fe_2Cl_6O$](THF)

| Atom | x | y | z | U(eq) | Atom | x | y | z | U(eq) |
|---|---|---|---|---|---|---|---|---|---|
| Fe(1) | 1942(1) | 2500 | 864(2) | 60(1) | N(4) | 3904(8) | 1538(15) | 9409(13) | 66(6) |
| Fe(2) | 627(1) | 2500 | 2396(2) | 54(1) | C(8) | 3101(16) | 1396(26) | 7728(24) | 83(11) |
| Cl(1) | 1726(3) | 2500 | -724(4) | 79(2) | C(9) | 3607(12) | 548(23) | 7930(20) | 88(8) |
| Cl(2) | 2504(2) | 1004(3) | 1223(3) | 99(1) | C(10) | 3771(15) | 480(21) | 9041(20) | 62(7) |
| Cl(3) | 1070(2) | 2500 | 3861(3) | 69(1) | C(11) | 4204(12) | 1553(22) | 10387(20) | 95(8) |
| Cl(4) | 11(2) | 1015(3) | 2245(3) | 91(1) | C(12) | 4027(14) | 2500 | 11065(22) | 67(9) |
| O(1) | 1198(8) | 2500 | 1481(13) | 135(7) | N(3A) | 4241(19) | 2500 | 9401(29) | 74(13) |
| N(1) | 3196(6) | 2500 | 4263(11) | 58(4) | N(4A) | 3610(21) | 1500(41) | 8206(32) | 138(17) |
| N(2) | 4050(4) | 1528(7) | 4951(7) | 57(3) | C(8A) | 3209(19) | 1598(34) | 7474(30) | 58(11) |
| C(1) | 3770(7) | 2500 | 4687(12) | 42(4) | C(9A) | 4189(25) | 397(38) | 9276(33) | 103(15) |
| C(2) | 2862(6) | 1496(10) | 4058(11) | 81(4) | C(10A) | 3561(21) | 522(38) | 8746(37) | 80(16) |
| C(3) | 3287(7) | 619(11) | 3875(12) | 99(5) | C(11A) | 4293(36) | 1201(66) | 10026(55) | 209(32) |
| C(4) | 3800(6) | 464(9) | 4639(10) | 69(4) | C(12A) | 3121(31) | 2500 | 7001(49) | 112(22) |
| C(5) | 4678(6) | 1513(10) | 5443(10) | 69(4) | O(1) | 370(10) | 2500 | 6613(13) | 160(8) |
| C(6) | 4823(9) | 2500 | 5994(14) | 82(6) | C(21) | 1414(12) | 1850(17) | 6547(14) | 144(8) |
| C(7) | 3686(8) | 2500 | 8934(12) | 54(4) | C(22) | 769(15) | 1508(18) | 6706(22) | 190(12) |
| N(3) | 3476(10) | 2500 | 8082(15) | 45(6) | | | | | |

### A.2.6 [TATC]$_2$[$Fe_2Cl_6$]($Et_2O$)

| Atom | x | y | z | U(eq) | Atom | x | y | z | U(eq) |
|---|---|---|---|---|---|---|---|---|---|
| Fe(1) | 3190(1) | 2812(1) | 768(1) | 40(1) | C(5) | 3289(6) | 714(10) | 3924(8) | 43(3) |
| Cl(1) | 3527(1) | 4682(2) | 917(2) | 40(1) | C(6) | 3917(6) | 467(12) | 4531(10) | 51(3) |
| Cl(2) | 2967(1) | 2328(2) | -845(2) | 42(1) | C(7) | 4450(6) | 1196(11) | 4231(10) | 49(3) |
| Cl(3) | 3738(2) | 1412(3) | 1638(2) | 53(1) | C(8) | 4830(6) | 3192(12) | 3978(11) | 59(4) |
| N(1) | 3489(5) | 3882(8) | 3647(7) | 43(2) | C(9) | 4597(9) | 4235(16) | 3367(15) | 39(7) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| N(2) | 3147(4) | 1964(8) | 3867(6) | 35(2) | C(9A) | 4659(9) | 4424(18) | 4166(20) | 53(9) |
| N(3) | 4258(5) | 2423(8) | 4093(7) | 43(2) | C(10) | 4002(5) | 4785(8) | 3597(8) | 50(3) |
| C(1) | 3643(5) | 2747(9) | 3816(7) | 33(2) | O(1) | 613(5) | 2866(8) | 2227(8) | 131(11) |
| C(2) | 2821(5) | 4324(10) | 3361(9) | 43(3) | C(11) | -105(5) | 2445(8) | 3460(8) | 162(12) |
| C(3) | 2342(6) | 3533(12) | 3715(10) | 54(3) | C(12) | 495(5) | 2419(8) | 3194(8) | 135(9) |
| C(4) | 2471(5) | 2289(10) | 3473(11) | 51(3) | | | | | |

### A.2.7 [PhTATC][$FeCl_3$-O-$FeCl_3$]

| Atom | x | y | z | U(eq) | Atom | x | y | z | U(eq) |
|---|---|---|---|---|---|---|---|---|---|
| Fe(1) | 3516(1) | 4412(1) | 2641(1) | 29(1) | C(13) | 12638(3) | 631(2) | 541(3) | 36(1) |
| Cl(1) | 1404(1) | 5415(1) | 3667(1) | 51(1) | C(14) | 12810(3) | 476(2) | 1426(3) | 46(1) |
| Cl(2) | 463(1) | 5239(1) | 1362(1) | 52(1) | C(15) | 12241(3) | 787(3) | 1951(3) | 51(1) |
| Cl(3) | 2961(1) | 3224(1) | 2902(1) | 53(1) | C(16) | 11497(3) | 1232(3) | 1600(3) | 44(1) |
| Cl(4) | 4266(1) | 4902(1) | 3883(1) | 53(1) | N(4) | 4758(2) | 3452(2) | -212(2) | 37(1) |
| Cl(5) | 4539(1) | 4238(1) | 1790(1) | 63(1) | N(5) | 5464(3) | 2367(3) | -1397(2) | 53(1) |
| Fe(2) | 1674(1) | 5608(1) | 2329(1) | 28(1) | N(6) | 5535(2) | 2361(2) | 471(2) | 29(1) |
| Cl(6) | 1921(1) | 6901(1) | 2172(1) | 43(1) | C(17) | 4767(3) | 4048(3) | -921(3) | 55(1) |
| O(1) | 2639(2) | 5058(2) | 2159(2) | 47(1) | C(18) | 4692(3) | 3641(3) | -1841(3) | 59(1) |
| N(1) | 10489(2) | 2630(2) | 753(2) | 26(1) | C(19) | 5425(4) | 3058(3) | -1980(3) | 60(1) |
| N(2) | 10512(2) | 2613(2) | -1118(2) | 33(1) | C(20) | 6331(3) | 1960(3) | -1154(3) | 52(1) |
| N(3) | 9722(2) | 1562(2) | -10(2) | 26(1) | C(21) | 6347(3) | 1434(3) | -374(3) | 45(1) |
| C(1) | 11327(2) | 3106(2) | 811(3) | 33(1) | C(22) | 6349(3) | 1861(2) | 488(3) | 39(1) |
| C(2) | 11388(3) | 3536(2) | -42(3) | 34(1) | C(23) | 4682(3) | 1914(2) | 438(3) | 38(1) |
| C(3) | 11392(3) | 3010(2) | -842(3) | 35(1) | C(24) | 3929(3) | 2484(3) | 521(3) | 49(1) |
| C(4) | 10479(3) | 1930(3) | -1707(2) | 39(1) | C(25) | 3865(3) | 3087(3) | -204(4) | 53(1) |
| C(5) | 9722(3) | 1337(3) | -1598(3) | 39(1) | C(26) | 5521(2) | 3101(2) | 153(2) | 25(1) |
| C(6) | 9768(3) | 956(2) | -687(3) | 34(1) | C(27) | 6388(2) | 3573(2) | 378(2) | 25(1) |
| C(7) | 8841(2) | 1978(2) | -92(3) | 37(1) | C(28) | 6866(3) | 3957(2) | -194(3) | 33(1) |
| C(8) | 8849(3) | 2538(2) | 667(3) | 38(1) | C(29) | 7632(3) | 4412(2) | 128(3) | 35(1) |
| C(9) | 9646(3) | 3099(2) | 684(3) | 33(1) | C(30) | 7927(3) | 4490(2) | 1010(3) | 39(1) |
| C(10) | 10468(2) | 1894(2) | 421(2) | 24(1) | C(31) | 7463(3) | 4097(2) | 1593(3) | 36(1) |
| C(11) | 11312(3) | 1399(2) | 703(2) | 27(1) | C(32) | 6700(2) | 3656(2) | 1278(2) | 31(1) |
| C(12) | 11887(2) | 1088(2) | 178(3) | 30(1) | | | | | |

### A.2.8 (PhTATC)$CuCl_2$

| Atom | x | y | z | U(eq) | Atom | x | y | z | U(eq) |
|---|---|---|---|---|---|---|---|---|---|
| Cu(1) | 2285(1) | 320(1) | 3373(1) | 18(1) | C(7) | 4021(3) | 2056(2) | 2580(2) | 22(1) |
| Cl(1) | 1328(1) | -1079(1) | 3981(1) | 26(1) | N(3) | 2701(3) | 1901(2) | 2985(1) | 18(1) |
| Cl(2) | 3043(1) | -614(1) | 2359(1) | 40(1) | C(8) | 1242(3) | 2324(2) | 2426(2) | 24(1) |
| C(1) | 2875(3) | 2274(2) | 3897(2) | 17(1) | C(9) | -132(4) | 1851(3) | 2706(2) | 29(1) |
| N(1) | 1628(3) | 1562(2) | 4107(1) | 18(1) | C(10) | 51(3) | 1926(3) | 3668(2) | 28(1) |
| C(2) | 1700(4) | 1302(2) | 5018(2) | 25(1) | C(11) | 2739(3) | 3524(2) | 4039(2) | 19(1) |
| C(3) | 3321(4) | 1013(2) | 5498(2) | 27(1) | C(12) | 3375(4) | 4298(2) | 3574(2) | 26(1) |
| C(4) | 4489(3) | 1812(2) | 5289(2) | 23(1) | C(13) | 3301(4) | 5422(3) | 3727(2) | 32(1) |
| N(2) | 4315(3) | 1779(2) | 4358(1) | 19(1) | C(14) | 2609(4) | 5818(3) | 4350(2) | 32(1) |
| C(5) | 5667(3) | 2165(2) | 4062(2) | 22(1) | C(15) | 2017(4) | 5072(3) | 4836(2) | 35(1) |
| C(6) | 5539(3) | 1724(2) | 3164(2) | 23(1) | C(16) | 2082(4) | 3943(3) | 4683(2) | 32(1) |

### A.2.9 [($^i$Pr$_3$TAC)Cu(PPh$_3$)]$BF_4$

| Atom | x | y | z | U(eq) | Atom | x | y | z | U(eq) |
|---|---|---|---|---|---|---|---|---|---|
| Cu(1) | 4155(1) | 5114(1) | 2527(1) | 31(1) | C(1) | 4487(3) | 7632(5) | 2592(2) | 27(1) |
| N(1) | 4597(2) | 6804(4) | 2203(2) | 26(1) | C(11) | 5259(3) | 7005(6) | 2000(2) | 34(1) |
| C(12) | 5416(3) | 5922(7) | 1682(3) | 55(2) | C(13) | 5343(3) | 8317(6) | 1775(2) | 46(2) |
| C(2) | 4029(3) | 6945(5) | 1899(2) | 28(1) | N(2) | 3478(2) | 6363(5) | 2145(2) | 27(1) |
| C(21) | 2910(3) | 5964(6) | 1867(2) | 36(1) | C(22) | 2504(3) | 7103(7) | 1688(2) | 52(2) |
| C(23) | 2478(4) | 5005(7) | 2123(3) | 58(2) | C(3) | 3329(3) | 7177(5) | 2538(2) | 30(1) |
| N(3) | 3920(2) | 7035(4) | 2821(2) | 25(1) | C(31) | 3831(3) | 7435(6) | 3294(2) | 32(1) |
| C(32) | 3843(4) | 8918(6) | 3364(2) | 56(2) | C(33) | 4329(3) | 6710(7) | 3578(2) | 44(2) |
| P(1) | 4233(1) | 3178(1) | 2781(1) | 26(1) | C(44) | 3816(3) | 3017(5) | 3318(2) | 26(1) |
| C(45) | 3245(3) | 3766(6) | 3382(2) | 37(1) | C(46) | 2910(3) | 3659(6) | 3780(2) | 40(2) |
| C(47) | 3126(3) | 2871(7) | 4111(2) | 44(2) | C(48) | 3701(3) | 2139(6) | 4057(2) | 37(1) |
| C(49) | 4030(3) | 2195(5) | 3657(2) | 30(1) | C(54) | 3823(3) | 1981(5) | 2429(2) | 27(1) |
| C(55) | 3209(3) | 1460(5) | 2531(2) | 33(1) | C(56) | 2873(3) | 686(6) | 2223(2) | 39(2) |
| C(57) | 3154(3) | 438(6) | 1817(2) | 46(2) | C(58) | 3777(4) | 900(7) | 1715(2) | 46(2) |
| C(59) | 4104(3) | 1683(6) | 2020(2) | 36(1) | C(64) | 5061(3) | 2563(6) | 2851(2) | 27(1) |
| C(65) | 5218(3) | 1221(6) | 2864(2) | 33(1) | C(66) | 5855(3) | 804(7) | 2924(2) | 47(2) |
| C(67) | 6350(3) | 1737(8) | 2974(2) | 54(2) | C(68) | 6216(3) | 3055(9) | 2967(2) | 54(2) |
| C(69) | 5567(3) | 3469(7) | 2903(2) | 41(2) | Cu(2) | 4975(1) | 3725(1) | -8(1) | 29(1) |
| C(4) | 4061(3) | 3574(5) | -641(2) | 27(1) | N(4) | 4318(2) | 2422(5) | -405(1) | 26(1) |
| C(41) | 4441(3) | 1265(5) | -694(2) | 31(1) | C(42) | 4949(3) | 382(6) | -487(2) | 47(2) |
| C(43) | 3816(3) | 496(6) | -821(2) | 45(2) | C(5) | 3893(3) | 2153(5) | -22(2) | 25(1) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| N(5) | 3983(2) | 3298(4) | 276(2) | 24(1) | C(51) | 3757(3) | 3059(6) | 740(2) | 34(1) |
| C(52) | 4071(3) | 4043(7) | 1045(2) | 43(2) | C(53) | 2998(3) | 3051(8) | 786(2) | 52(2) |
| N(6) | 4156(2) | 4662(4) | -328(2) | 26(1) | C(6) | 3732(3) | 4472(5) | 59(2) | 28(1) |
| C(61) | 4118(3) | 6027(6) | -516(2) | 33(1) | C(62) | 3460(3) | 6311(7) | -747(3) | 51(2) |
| C(63) | 4681(3) | 6263(6) | -830(2) | 49(2) | P(2) | 5947(1) | 3878(1) | 255(1) | 26(1) |
| C(70) | 6537(2) | 2984(6) | -91(2) | 27(1) | C(71) | 6619(3) | 1642(5) | -29(2) | 35(1) |
| C(72) | 6960(3) | 929(7) | -345(2) | 41(2) | C(73) | 7229(3) | 1509(7) | -710(2) | 43(2) |
| C(74) | 7161(3) | 2848(7) | -763(2) | 44(2) | C(75) | 6812(3) | 3601(6) | -460(2) | 36(1) |
| C(80) | 6268(3) | 5528(5) | 329(2) | 31(1) | C(81) | 6937(3) | 5825(6) | 362(2) | 37(1) |
| C(82) | 7131(3) | 7097(7) | 442(2) | 46(2) | C(83) | 6675(4) | 8079(7) | 485(2) | 50(2) |
| C(84) | 6012(4) | 7806(6) | 460(2) | 48(2) | C(85) | 5805(3) | 6541(6) | 370(2) | 38(2) |
| C(90) | 6002(3) | 3108(5) | 802(2) | 28(1) | C(91) | 6424(3) | 3485(6) | 1132(2) | 33(1) |
| C(92) | 6418(3) | 2854(7) | 1539(2) | 43(2) | C(93) | 5990(3) | 1832(7) | 1617(2) | 42(2) |
| C(94) | 5580(3) | 1412(6) | 1284(2) | 42(2) | C(95) | 5578(3) | 2034(6) | 881(2) | 36(1) |
| B(1) | 6631(4) | 7072(8) | 3102(3) | 43(2) | F(1) | 6713(3) | 6702(6) | 2678(2) | 92(2) |
| F(2) | 5976(2) | 7241(7) | 3195(2) | 99(2) | F(3) | 6865(4) | 6108(6) | 3375(2) | 121(2) |
| F(4) | 6971(2) | 8185(5) | 3201(2) | 81(2) | B(2) | 4000(4) | 8648(8) | 624(2) | 41(2) |
| F(5) | 3772(3) | 8708(6) | 212(2) | 106(2) | F(6) | 4510(2) | 9508(5) | 699(2) | 75(1) |
| F(7) | 4154(5) | 7436(7) | 721(4) | 196(5) | F(8) | 3509(3) | 8998(10) | 892(3) | 188(5) |

### A.2.10 $[(\mathbf{Bz_3TAC})\mathbf{CuPPh_3}][\mathbf{BF_4}] \cdot \mathbf{0.5\,Tol}$.

| Atom | x | y | z | U(eq) | Atom | x | y | z | U(eq) |
|---|---|---|---|---|---|---|---|---|---|
| Cu | 3577(1) | 2421(1) | 7495(1) | 31(1) | P | 4218(1) | 3907(1) | 6964(1) | 25(1) |
| C(1) | 2044(4) | 1311(3) | 8374(2) | 34(1) | N(1) | 3731(3) | 934(2) | 8178(1) | 30(1) |
| C(10) | 4665(4) | 524(3) | 8753(2) | 39(1) | C(11) | 4613(4) | 1507(3) | 9177(2) | 34(1) |
| C(12) | 5313(4) | 2413(3) | 8945(2) | 45(1) | C(13) | 5241(5) | 3333(4) | 9342(3) | 65(1) |
| C(14) | 4479(6) | 3329(4) | 9973(3) | 72(1) | C(15) | 3820(5) | 2437(4) | 10203(2) | 63(1) |
| C(16) | 3879(4) | 1536(3) | 9806(2) | 47(1) | C(2) | 1581(4) | 1013(3) | 7274(2) | 38(1) |
| N(2) | 1372(3) | 1893(2) | 7769(1) | 29(1) | C(20) | -284(4) | 2542(3) | 7894(2) | 40(1) |
| C(21) | -432(3) | 3613(3) | 8269(2) | 32(1) | C(22) | -170(4) | 4638(3) | 7945(2) | 40(1) |
| C(23) | -238(4) | 5615(3) | 8287(2) | 50(1) | C(24) | -574(5) | 5580(4) | 8952(2) | 56(1) |
| C(25) | -836(5) | 4569(4) | 9287(2) | 59(1) | C(26) | -772(4) | 3588(3) | 8945(2) | 47(1) |
| C(3) | 3998(4) | 17(3) | 7712(2) | 38(1) | N(3) | 3268(3) | 581(2) | 7118(1) | 34(1) |
| C(30) | 3616(4) | -250(3) | 6588(2) | 47(1) | C(31) | 3270(4) | 341(3) | 5923(2) | 41(1) |
| C(32) | 2222(4) | 28(4) | 5558(2) | 54(1) | C(33) | 2001(5) | 504(4) | 4925(2) | 67(1) |
| C(34) | 2794(5) | 1320(4) | 4646(2) | 62(1) | C(35) | 3821(5) | 1651(4) | 5001(2) | 55(1) |
| C(36) | 4058(4) | 1158(3) | 5635(2) | 45(1) | C(41) | 4774(4) | 4995(3) | 7396(2) | 30(1) |
| C(42) | 3994(4) | 5290(3) | 8002(2) | 41(1) | C(43) | 4324(5) | 6184(3) | 8332(2) | 52(1) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C(44) | 5431(5) | 6744(3) | 8057(2) | 54(1) | C(45) | 6228(5) | 6455(3) | 7464(2) | 54(1) |
| C(46) | 5899(4) | 5588(3) | 7128(2) | 44(1) | C(51) | 2563(3) | 4756(3) | 6527(1) | 25(1) |
| C(52) | 1895(4) | 5949(3) | 6594(1) | 29(1) | C(53) | 510(4) | 6497(3) | 6318(2) | 35(1) |
| C(54) | -193(4) | 5856(3) | 5965(2) | 38(1) | C(55) | 473(4) | 4675(3) | 5890(2) | 39(1) |
| C(56) | 1834(4) | 4122(3) | 6170(2) | 32(1) | C(61) | 5808(3) | 3436(2) | 6333(1) | 26(1) |
| C(62) | 5919(4) | 4034(3) | 5723(2) | 35(1) | C(63) | 7150(4) | 3611(3) | 5259(2) | 41(1) |
| C(64) | 8274(4) | 2590(3) | 5408(2) | 40(1) | C(65) | 8177(4) | 1998(3) | 6020(2) | 37(1) |
| C(66) | 6948(3) | 2411(3) | 6480(2) | 30(1) | B | 1463(5) | 10881(4) | 2514(3) | 55(1) |
| F(1) | 1843(3) | 9733(2) | 2347(1) | 61(1) | F(2) | 2151(4) | 11517(2) | 1982(2) | 92(1) |
| F(3) | -79(3) | 11403(2) | 2523(2) | 94(1) | F(4) | 2216(4) | 11022(3) | 3025(2) | 112(1) |
| C(71) | 1154(5) | 9540(4) | 268(3) | 62(1) | C(72) | 786(11) | 10354(8) | 769(4) | 60(2) |
| C(73) | -609(9) | 11324(5) | 714(3) | 91(2) | C(74) | 1533(12) | 8695(10) | -242(8) | 98(5) |
| C(75) | -241(11) | 10481(7) | 191(4) | 60(2) | | | | | |

### A.2.11 $(Me_3TAC)_2CuCl_2 \cdot (C_7H_8)_{0.5}$

| Atom | x | y | z | U(eq) | Atom | x | y | z | U(eq) |
|---|---|---|---|---|---|---|---|---|---|
| Cu | 794(1) | 468(1) | 2605(1) | 37(1) | Cl(1) | -824(2) | 1407(1) | 1805(1) | 50(1) |
| Cl(2) | 1951(2) | 1346(1) | 3596(1) | 50(1) | C(1) | 2138(6) | 43(4) | 1366(2) | 47(1) |
| N(1) | 2630(5) | 586(2) | 2032(2) | 40(1) | C(11) | 3326(6) | 1566(3) | 1884(3) | 52(1) |
| C(2) | 3721(5) | -49(3) | 2481(3) | 45(1) | N(2) | 2798(5) | -887(3) | 2693(2) | 45(1) |
| C(21) | 3648(7) | -1481(4) | 3271(3) | 69(2) | C(3) | 2257(6) | -1475(3) | 2058(3) | 53(1) |
| N(3) | 1281(5) | -826(3) | 1592(2) | 47(1) | C(31) | 542(7) | -1367(4) | 967(3) | 76(2) |
| C(4) | -245(5) | -879(3) | 3664(2) | 39(1) | N(4) | -909(4) | -210(2) | 3091(2) | 34(1) |
| C(41) | -1896(6) | -806(4) | 2540(2) | 45(1) | C(5) | -1838(5) | 569(3) | 3423(2) | 41(1) |
| N(5) | -3001(4) | 119(3) | 3831(2) | 42(1) | C(51) | -3837(6) | 917(4) | 4164(3) | 57(1) |
| C(6) | -2288(6) | -532(3) | 4393(2) | 47(1) | N(6) | -1438(5) | -1326(3) | 4056(2) | 41(1) |
| C(61) | -751(6) | -2016(4) | 4614(2) | 53(1) | C(10) | 3891(20) | 3992(18) | 4467(8) | 88(4) |
| C(20) | 3929(12) | 5064(12) | 4557(5) | 102(4) | C(30) | 3823(44) | 6022(61) | 4626(23) | 312(45) |
| C(40) | 4995(21) | 6569(10) | 5085(9) | 156(5) | C(50) | 4917(30) | 5614(14) | 4969(11) | 118(8) |

### A.2.12 $(Me_3TAC)_6(CuCl_3)_2(Cu_2Cl_4)$

| Atom | x | y | z | U(eq) | Atom | x | y | z | U(eq) |
|---|---|---|---|---|---|---|---|---|---|
| Cu(1) | 1071(1) | 2199(1) | 12089(1) | 45(1) | Cl(1) | 1182(1) | 983(1) | 12419(3) | 54(1) |
| Cl(2) | 1003(1) | 3451(1) | 12054(3) | 53(1) | Cu(2) | 699(1) | 1442(1) | 9603(2) | 53(1) |
| Cl(3) | 316(1) | 1230(2) | 11098(3) | 56(1) | Cl(5) | 1092(1) | 6990(2) | 2322(3) | 54(1) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Cl(6) | 1048(1) | 6989(1) | -2387(2) | 47(1) | Cl(7) | 378(1) | 6169(1) | 399(3) | 47(1) |
| Cl(4) | 994(1) | 1631(2) | 7631(3) | 58(1) | Cu(3) | 835(1) | 6737(1) | 7(1) | 45(1) |
| Cu(4) | 2460(1) | 9808(1) | 2351(1) | 37(1) | Cl(8) | 2605(1) | 11113(1) | 2347(3) | 44(1) |
| Cl(9) | 2844(1) | 8912(1) | 2228(3) | 42(1) | Cl(10) | 1972(1) | 9445(2) | 2451(4) | 57(1) |
| N(1) | -107(2) | 1286(5) | 16563(9) | 48(2) | N(2) | 301(2) | 2121(4) | 15580(8) | 41(2) |
| N(3) | 351(2) | 750(4) | 15438(8) | 40(2) | N(4) | 1075(2) | 4491(4) | 6960(8) | 40(2) |
| N(5) | 1433(2) | 5107(4) | 8757(7) | 38(2) | N(6) | 1521(2) | 5190(5) | 6031(8) | 37(2) |
| N(7) | 391(1) | 5641(4) | 4850(8) | 33(1) | N(8) | -44(2) | 6129(4) | 6278(9) | 44(2) |
| N(9) | 343(2) | 6993(4) | 5256(8) | 36(2) | N(10) | 2441(1) | 6985(4) | 2280(9) | 35(1) |
| N(11) | 1973(2) | 7360(4) | 993(7) | 34(2) | N(12) | 1999(2) | 7353(4) | 3757(7) | 36(2) |
| N(13) | 1322(2) | 9295(4) | 8850(8) | 36(2) | N(14) | 1684(2) | 10124(4) | 7420(9) | 41(2) |
| N(15) | 1327(2) | 9261(4) | 6070(8) | 38(2) | N(16) | 1872(2) | 12222(5) | 3543(8) | 40(2) |
| N(17) | 1928(2) | 13511(4) | 2318(9) | 41(2) | N(18) | 1872(2) | 12287(5) | 795(9) | 42(2) |
| C(1) | 110(2) | 639(5) | 16646(11) | 46(2) | C(2) | 55(2) | 2034(5) | 16779(11) | 45(2) |
| C(3) | 432(2) | 1469(5) | 15047(11) | 40(2) | C(4) | 1197(2) | 4991(6) | 5694(10) | 43(2) |
| C(5) | 1113(2) | 4868(5) | 8493(10) | 38(2) | C(6) | 1609(2) | 5242(4) | 7526(10) | 33(2) |
| C(7) | 464(2) | 6373(5) | 4518(9) | 31(2) | C(8) | 169(2) | 5468(5) | 6143(10) | 41(2) |
| C(9) | 119(2) | 6867(5) | 6542(10) | 43(2) | C(10) | 2334(2) | 7361(6) | 3704(10) | 42(2) |
| C(11) | 2311(2) | 7376(6) | 880(10) | 42(2) | C(12) | 1843(2) | 7368(4) | 2389(10) | 34(2) |
| C(13) | 1252(2) | 8962(4) | 7501(10) | 34(2) | C(14) | 1502(2) | 10056(6) | 8840(10) | 41(2) |
| C(15) | 1491(2) | 10022(5) | 5997(10) | 41(2) | C(16) | 1887(2) | 11883(5) | 2119(11) | 39(2) |
| C(17) | 1808(2) | 13084(5) | 3668(10) | 41(2) | C(18) | 1811(2) | 13170(5) | 853(10) | 40(2) |
| C(10A) | -299(2) | 1252(7) | 15113(16) | 70(3) | C(20) | 414(2) | 2919(5) | 15188(13) | 54(2) |
| C(30) | 514(2) | 57(5) | 14854(12) | 53(2) | C(40) | 1198(2) | 3660(5) | 6910(12) | 48(2) |
| C(50) | 1535(3) | 5225(6) | 10405(9) | 50(2) | C(60) | 1723(2) | 5321(5) | 4692(10) | 43(2) |
| C(70) | 509(2) | 4971(5) | 3920(10) | 41(2) | C(80) | -259(2) | 6158(6) | 4943(14) | 56(2) |
| C(90) | 461(2) | 7803(4) | 4997(11) | 41(2) | C(100) | 2400(2) | 6110(5) | 2257(14) | 49(2) |
| C(110) | 1793(2) | 7368(6) | -481(10) | 48(2) | C(120) | 1842(2) | 7429(7) | 5284(10) | 53(3) |
| C(130) | 1222(2) | 8976(6) | 10375(10) | 47(2) | C(140) | 1954(2) | 9609(5) | 7418(14) | 54(2) |
| C(150) | 1247(2) | 8860(5) | 4588(10) | 44(2) | C(160) | 1878(2) | 11740(7) | 5018(12) | 61(3) |
| C(170) | 2262(2) | 13571(6) | 2320(14) | 58(2) | C(180) | 1858(3) | 11901(7) | -763(12) | 63(3) |

### A.2.13 ($^{t}$Bu$_2$TACCH$_2$)-mC$_6$H$_4$-(CH$_2$TAC$^{t}$Bu$_2$)

| Atom | x | y | z | U(eq) | Atom | x | y | z | U(eq) |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 6478(16) | -1685(17) | 14094(13) | 39(4) | N(1) | 5841(10) | -3117(14) | 13629(11) | 46(4) |
| C(11) | 4519(14) | -3828(15) | 13993(12) | 34(4) | C(12) | 4108(14) | -5320(19) | 13654(16) | 67(6) |
| C(13) | 4450(20) | -3370(20) | 15046(16) | 72(7) | C(14) | 3502(18) | -3580(20) | 13230(16) | 64(6) |
| C(2) | 6807(15) | -3646(14) | 13951(13) | 39(4) | N(2) | 8083(13) | -3014(14) | 13473(10) | 39(4) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C(21) | 8986(15) | -3632(16) | 13507(12) | 35(4) | C(22) | 8385(18) | -4992(19) | 12899(13) | 56(5) |
| C(23) | 9713(19) | -3482(18) | 14552(18) | 68(6) | C(24) | 10267(16) | -2880(20) | 13069(16) | 69(7) |
| C(3) | 8531(14) | -1640(15) | 13866(12) | 32(4) | N(3) | 7624(14) | -1106(15) | 13661(10) | 48(4) |
| C(31) | 7361(14) | -1153(15) | 12643(10) | 36(4) | C(32) | 8618(16) | -326(16) | 12210(12) | 39(4) |
| C(33) | 9146(17) | 1062(17) | 12663(12) | 41(4) | C(34) | 10245(17) | 1867(13) | 12346(12) | 44(5) |
| C(35) | 10799(18) | 1381(15) | 11576(12) | 46(5) | C(36) | 10961(16) | -536(13) | 10394(11) | 33(4) |
| C(37) | 10290(14) | -8(18) | 11132(11) | 39(4) | C(38) | 9183(16) | -758(15) | 11501(11) | 31(4) |
| C(4) | 11969(17) | -255(17) | 8872(13) | 45(5) | N(4) | 11167(12) | 153(10) | 9592(8) | 26(3) |
| C(5) | 9858(17) | -57(16) | 9020(14) | 47(5) | N(5) | 9191(11) | -1436(13) | 8424(9) | 33(3) |
| C(51) | 7708(14) | -1846(17) | 8006(11) | 33(4) | C(52) | 7680(20) | -1060(20) | 7343(16) | 62(6) |
| C(53) | 7187(17) | -3250(20) | 7480(15) | 76(7) | C(54) | 6911(16) | -1640(20) | 8899(12) | 49(5) |
| C(6) | 10103(17) | -1627(19) | 7746(13) | 47(5) | N(6) | 11312(12) | -1557(14) | 8305(10) | 38(4) |
| C(61) | 12166(18) | -2072(18) | 7633(13) | 43(5) | C(62) | 11316(19) | -3396(17) | 6991(15) | 50(5) |
| C(63) | 13228(18) | -2091(19) | 8289(16) | 61(6) | C(64) | 12812(14) | -1207(18) | 6933(14) | 51(5) |
| C(7) | 7910(19) | 2215(16) | 9520(15) | 57(6) | N(7) | 8434(14) | 3649(10) | 9863(9) | 31(3) |
| C(71) | 9845(19) | 4270(20) | 9670(15) | 51(5) | C(72) | 10763(19) | 3980(20) | 10131(16) | 68(6) |
| C(73) | 9930(20) | 3890(20) | 8582(18) | 81(8) | C(74) | 10216(18) | 5749(15) | 9886(13) | 49(5) |
| C(8) | 7373(16) | 4025(18) | 9651(11) | 45(5) | N(8) | 6227(11) | 3525(11) | 10103(9) | 23(3) |
| C(81) | 5180(17) | 4120(20) | 10114(16) | 53(5) | C(82) | 4680(20) | 4010(20) | 9073(13) | 68(6) |
| C(83) | 5989(18) | 5613(16) | 10582(17) | 57(6) | C(84) | 4151(16) | 3502(18) | 10716(12) | 43(4) |
| C(9) | 5523(15) | 2007(15) | 9699(13) | 38(4) | N(9) | 6592(12) | 1531(11) | 9918(10) | 37(4) |
| C(91) | 6855(19) | 1638(19) | 10987(14) | 71(7) | C(92) | 5084(16) | -581(15) | 10940(12) | 35(4) |
| C(93) | 3991(13) | -1464(17) | 11331(11) | 37(4) | C(94) | 3428(14) | -897(16) | 12058(12) | 37(4) |
| C(95) | 3953(19) | 437(16) | 12438(12) | 42(5) | C(96) | 3407(18) | 1120(20) | 13309(13) | 71(7) |
| C(97) | 5052(16) | 1275(18) | 12094(12) | 42(4) | C(98) | 5672(14) | 690(17) | 11298(11) | 29(4) |
| C(10) | 2251(15) | 715(16) | 14742(11) | 44(5) | N(10) | 3104(13) | 388(17) | 14084(11) | 55(4) |
| C(110) | 4332(13) | 562(14) | 14583(9) | 24(3) | N(11) | 5062(13) | 1886(12) | 15144(10) | 42(4) |
| C(111) | 6448(18) | 2216(17) | 15582(16) | 56(5) | C(112) | 7198(15) | 2050(20) | 14769(16) | 76(7) |
| C(113) | 6604(19) | 1330(20) | 16322(15) | 71(6) | C(114) | 7140(17) | 3732(17) | 16148(14) | 64(6) |
| C(120) | 4265(14) | 2244(15) | 15902(11) | 30(4) | N(12) | 2973(11) | 2110(11) | 15398(9) | 30(3) |
| C(121) | 2088(16) | 2499(16) | 15975(13) | 40(4) | C(122) | 1420(20) | 1643(19) | 16660(14) | 64(6) |
| C(124) | 984(17) | 2630(20) | 15362(14) | 67(6) | C(123) | 2928(19) | 3962(17) | 16587(12) | 56(6) |

### A.2.14 $(\mathbf{HTATC})_2(\mathbf{TATC})[(\mathbf{Me_3SiCH_2})_2\mathbf{Cr}(\mathbf{CSiMe_3})]_2$

| Atom | x | y | z | U(eq) | Atom | x | y | z | U(eq) |
|---|---|---|---|---|---|---|---|---|---|
| Cr(1) | 60(1) | 4658(1) | 558(1) | 40(1) | C(20) | 218(5) | 3182(4) | 799(3) | 47(1) |
| Si(1) | 138(1) | 2110(1) | 265(1) | 40(1) | C(21) | 1275(5) | 2087(6) | -236(3) | 63(2) |
| C(22) | -1209(5) | 2089(5) | -245(3) | 61(2) | C(23) | 233(6) | 904(5) | 721(3) | 59(2) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C(30) | 72(9) | 5557(5) | 1314(3) | 87(3) | Si(2) | -314(2) | 5136(1) | 2019(1) | 78(1) |
| C(31) | -518(9) | 6114(6) | 2583(4) | 96(3) | C(32) | 709(14) | 4255(12) | 2413(7) | 88(5) |
| C(33) | -1565(16) | 4247(16) | 1951(9) | 116(7) | C(32A) | -253(18) | 3996(15) | 2334(9) | 89(7) |
| C(33A) | -1986(27) | 4958(28) | 1676(17) | 184(15) | C(40) | -1101(5) | 4934(4) | -50(3) | 47(2) |
| Si(3) | -2651(2) | 4931(2) | -169(1) | 89(1) | C(41) | -3250(13) | 3917(12) | 287(8) | 90(5) |
| C(42) | -3130(18) | 4235(17) | -947(9) | 133(8) | C(43) | -3344(16) | 6028(15) | -176(9) | 122(7) |
| C(41A) | -3178(15) | 5879(14) | -789(8) | 84(6) | C(42A) | -3207(17) | 5795(16) | 495(9) | 98(7) |
| C(43A) | -3404(21) | 3891(19) | -291(13) | 131(9) | C(1) | -637(4) | 10102(4) | 3797(2) | 35(1) |
| N(1) | -53(3) | 9148(3) | 3744(2) | 36(1) | C(2) | 927(5) | 9057(5) | 4203(3) | 47(1) |
| C(3) | 1726(5) | 9913(5) | 4149(3) | 52(2) | C(4) | 1115(5) | 10897(5) | 4190(3) | 47(1) |
| N(2) | 131(3) | 10936(3) | 3730(2) | 38(1) | C(5) | -423(5) | 11911(4) | 3772(3) | 55(2) |
| C(6) | -1417(6) | 11996(5) | 3297(3) | 61(2) | C(7) | -2187(5) | 11119(5) | 3365(3) | 53(2) |
| N(3) | -1589(3) | 10162(3) | 3326(2) | 39(1) | C(8) | -2378(5) | 9338(5) | 3366(3) | 51(2) |
| C(9) | -1801(5) | 8338(4) | 3328(3) | 53(2) | C(10) | -798(5) | 8289(4) | 3813(3) | 48(1) |
| C(11) | 2500 | -112(6) | 2500 | 40(2) | N(4) | 1532(4) | 386(4) | 2372(2) | 42(1) |
| C(12) | 1474(6) | 1475(5) | 2436(4) | 56(2) | C(13) | 2500(10) | 1926(9) | 2178(6) | 56(3) |
| N(5) | 2500 | -1123(5) | 2500 | 52(2) | C(14) | 453(5) | -132(5) | 2267(3) | 47(2) |
| C(15) | 597(5) | -1136(5) | 1985(3) | 61(2) | C(16) | 1454(6) | -1707(5) | 2371(4) | 69(2) |

# References


[1] K.Hock, *Ger.*, **1904**, *139*, 394; L.Kahovec, *Z. Physik. Chem.*, **1939**, *B43*, 364; L. Henry, *Bull. Acad. Belg.*, (3), **1893**, *26*, 200; L. Henry, *Bull. Acad. Belg.*, (3), **1895**, *29*, 23; A. Francimont, H. Van Erp, *Rec. trav. chim*, **1896**, *15*, 66; J. Graymore, *J. Chem. Soc.*, **1932**, 1353

[2] **a)** E. M. Smolin, L.Rapoport "s-Triazines and Derivatives" in "The Chemistry of Heterocyclic Compounds", Interscience Publischer Ltd., London **1959**, 473 and Ref.; **b)** E. D. Bergemann, A.Kaluszyner, *Recl. Trav. Chim.*, Pays-Bas **1969** , *78*, 315; **c)** H. Linde, H.Oelschl"ager, C. Czirwitzky., *Arzneim. Forsch.* **1978**, *28*, 973; **d)** BEILSTEIN, "Handbook of Organic Chemistry", 4th Ed. Vth Suppl. Series, Springer-Verlag, Berlin, Vol. **26**, **1986**, pp. 3 and Ref.

[3] **a)** D. C. Bradley, D. M. Frigo, I. S. Harding, M. B. Hursthouse, M. Montevalli, *J. Chem. Soc*, *Chem. Commun.*, **1992**, 577; **b)** D. C. Bradley, H. Dawes, D. M. Frigo, M. B. Hursthouse, B. Hussain, *J. Organomet. Chem.*, **1987**, *325*, 55

[4] M. Westerhausen, W. Schwarz, *J. Organomet Chem.*, **1993**, *463*, 51

[5] W. Uhl, M. Koch, S. Pohl, W. Saak, *Z. Anorg. Allg. Chem.*, **1994**, *620*, 1619

[6] A. Lüttinghaus, W. Kullick, *Tetrahedron Lett.*, **1959**, 13

[7] H. Werner, *J. Organomet. Chem.*, **1966**, *5*, 100

[8] M. B. Hursthouse, M. Motevall, P. O'Brien, J.R. Walsh, *Organometallics*, **1991**, *10*, 3196

[9] R. Fuchs, P. Klüfers, *J. Organomet. Chem.*, **1992**, *424*, 353

[10] Murray V. Baker, Maria C. Palermo, Brian W. Skelton, Allan H. White, *Aust. J. Chem.*, **1999**, *52*, 170

[11] Paul J. Wilson, Paul A. Cooke, Alexander J. Blake, Philip Mountford, Martin Schröder, *New J. Chem.*, **1999**, 271

[12] R. D. Köhn, Habil. paper, TU-Berlin **1996**

[13] M. Haufe, R. D. Köhn, R. Weiman, G. Seifert, D. Zeigan, *J. Organometal. Chem.*, **1996**, *520*, 121

[14] M. Haufe, Randolf D. Köhn, Gabriele Kociok-Köhn, Alexander C. Filipou, *Inorg. Chem. Comm.*, **1998**, *1*, 263

[15] Y. Nomura, K. Ogawa, Y. Takeuchi, S. Tomoda, *Chem. Lett.*, **1977**, 693

[16] Steven P. van Kouventberg, Edward H. Wong, Gary Weisman, Eric J. Gabe, Florence L. Lee, Pete Jackson, *Polyhedron Vol. 8*, **1989**, *19*, 2333

[17] Kenneth D. Karlin, Yilma Gulneh, *Prog. Inorg. Chem.*, **1987**, *35*, 219

[18] S. Mahapatra, V. G. Young Jr., S. Kaderli, A. D. Zuberbuehler, William B. Tolman, *Angew. Chem.*, **1997**, *109*, 109

[19] G. R. Weisman, V. Johnson, R. E. Fiala, *Tetrahedron Lett.*, **1980**, *21*, 3635

[20] T.J. Atkins, *J. Am. Soc.*, **1980**, *102*, 6364

[21] Roger W. Alder, Rodney W. Mowlam, David J. Vachon and Gary R. Weisman, *A. Chem. Soc. Chem Commun.*, **1992**, 507

[22] J. M. Erhardt, J. D. Wuest, *J. Am. Chem. Soc.*, **1980**, *102*, 6363

[23] J. M. Erhardt, E. R. Grover, J. D. Wuest, *J. Am. Chem. Soc.*, **1980**, *102*, 6365

[24] J. Chatt, L. Manjiliović-Muir, K. Muir, *Chem Commun.*, **1991**, 655; J. M. Mayer, *Angew. Chem.*, **1992**, *104*, 293; *Angew. Chem. Int. Ed. Engl.*, **1992**, *31*, 286 and references therein.

[25] W. D. Stohrer, R. Hoffmann, *J.Am.Chem.Soc.*, **1972**, *94*, 1661

[26] R. D. Köhn, Guido Seifert, G. Kociok-Köhn, *Angew. Chem. Int. Ed. Engl.*, **1996**, *35*, 2879

[27] M. Pasquali, C. Floriani, A. Gaetani-Manfredotti, A. Chiesi-Villa, *J. Am. chem. Soc.*, **1978**, *100*, 4918

[28] W. E. Broderick, K. Kanamori, R. D. Willett, J. I. Legg, *Inorg. Chem.*, **1991**, *30*, 3875

[29] R. D. Köhn, Guido Seifert, G. Kociok-Köhn, *Chem. Ber.*, **1996**, *129* 1327

[30] H. Brunner, A. Winter, B. Nuber, *J. Organomet. Chem*, **1998**, *558*, 213

[31] E. I. Solomon, M. J. Baldwin, M. D. Lowery, *Chem. Rev.*, **1992**, *92*, 521

[32] W. Kaim, J. Rall, *Angew. Chem.*, **1996**, *108*, 47

[33] H. Stegeman, A. Oprea, K. F. Tebbe, *Z. Anorg. Allg. Chem.*, **1995**, *621*, 871

[34] C. Clegg, J. R. Nicholson, D. Collison, C. D. Garner, *Acta Crystallogr., Sect. C*, **1988**, *44*, 543

[35] S. Andersson, S. Jagner, *Acta Chem. Scand. Ser. A*, **1988**, *42*, 691

[36] See, for example: **a)** P. Pyykkö, *Chem. Rev.*, **1997**, *97*, 597; **b)** Unkonventionelle Wechselwirkungen in der Chemie metallischer Elemente, ed. B. Krebs, VCH, Weinheim, **1992**

[37] H. Schmidbaur, *Gold Bull.*, **1990**, *23*, 11

[38] D. E. Harwell, M. D. Mortimer, C. B. Knobler, F. A. L. Anet, M. F. Hawthorne, *J. Am. Chem. Soc.*, **1996**, *118*, 2679

[39] U. Simeling, U. Vorfeld, B. Neumann, H. G. Stammler, *Chem. Commun.*, **1997**, 1723

[40] T. Yamaguchi, O. Lindqvist, *Acta. Chem. Scand. Ser. A.*, **1983**, *37*, 685; G. W. Eastland, M. M. Mazid, D. R. Russel, M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, **1980**, 1682; P. W. R. Corfield, H. M. M. Shearer, *Acta Crystallogr.*, **1966**, *20*, 502

[41] K. Singh, J. R. Long, P. Stavropoulos, *J. Am. Chem. Soc.*, **1997**, *119*, 2942

[42] J.-M. Poblet, M. Bénard, *Chem. Comm.*, **1998**, *11*, 1179

[43] N. Kitajima, T. Koda, S. Hashimoto, T. Kitagawa, Y. Moro-oka, *J. Am. Chem. Soc.*, **1991**, *113*, 5664

[44] E. W. Ainscough, A. M. Brodie, S. L. Ingham, J. M. Waters, *J. Chem. Soc., Dalton Trans.*, **1994**, 215

[45] Z. Tyeklár, R. R. Jacobson, N. Wei, N. N. Murthy, J. Zubieta, K. D. Karlin, *J. Am. Chem. Soc.*, **1993**, *115*, 2677

[46] R. D. Köhn, G. Kociok-Köhn, M. Haufe, *J. Organomet. Chem.*, **1995**, *501*, 303

[47] L. T. J. Delbaere, D. W. McBride, R. B. Ferguson, *Acta Crystallogr., Sect. B*, **1970**, *26*, 515

[48] F. Olbrich, G.Schmidt, E. Weiss, U. Behrens, *J. Organomet. Chem.*, **1993**, *456*, 299

[49] F. A. Cotton, J. Takats, *J.Am.Chem.Soc.*, **1970**, *92*, 2353

[50] Murrray V. Baker, D. H. Brown, B. W. Skelton, Allan H. White, *J. Chem. Soc., Dalton Trans.*, **1999**, 1483

[51] Steven D. R. Christie, Kwok W. Man, Richard J. Whitby, Alexandra M. Z. Slawin, *Organometallics*, **1999**, *18*, 348

[52] Y.-X. Chen, T. J. Marks, *Organometallics*, **1997**, *16*, 3649

[53] Gielens, E. E. G.; Tiesnitsch, J. Y.; Hessen, B.; Teuben, J. H., *Organometallics*, **1998**, *17*, 1652

[54] G. Bhandari, Y. Kim, J. M. McFarland, A. L. Rheingold, K. H. Theopold, *Organometallics*, **1995**, *14*, 738

[55] R. Emrich, O. Heinemann, P.W. Jolly, C. Krüger, G. P. J. Verhovnik, *Organometallics*, **1997**, *16*, 1511

[56] P. W. Jolly, K. Jonas, G. P. J. Verhovnik, A. Dohring, J. Gohre, J. C. Weber (Studiengesellschaft Kohle m.b.H.), WO-A 98/04570, **1998** [Chem. Abstr. 1998. 128, 167817v].

[57] R. D. Köhn, private communication

[58] Jason A. Halfen, Victor G. Young, Jr., William B. Tolman, *J. Am. Chem. Soc.*, **1996**, *118*, 10920

[59] Scott E. Watkins, Xinhao Yang, Donald C. Craig, Stephen B. Colbran, *J. Chem. Soc., Dalton Trans.*, **1999**, 1539

[60] Y. Ishii, K. Miyashita, K. Kamita, M. Hidai, *J. Am. Chem. Soc.*, **1997**, *119*, 6448

[61] *Appel, Angew. Chem. Int. Ed. Engl.*, **1975** *14*, 801; [*Angew. Chem.*, *87*, 863]

[62] Robert A. Egli, *Helv. Chim. Acta*, **1970**, *53*, 47

[63] R. A. Heintz, R. L. Ostrander, A. L. Rheingold, K. H. Theopold, *J. Am. Chem. Soc.*, **1994**, *116*, 11387

[64] A. A. Danapoulos, G. Wilkinson, T. K. N. Sweet, M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, **1995**, 2111

[65] S. K. Noh, S. C. Sendlinger, C. Janiak, K. H. Theopold, *J. Am. Chem. Soc.*, **1989**, *111*, 9127

[66] S. K. Noh, R. A. Heintz, C. Janiak, S. C. Sendlinger, K. H. Theopold, *Angew. Chem. Int. E. Engl.*, **1990**, *29*, 775

[67] M. B. Hursthouse, K. M. A. Malik, K. D. Sales, *J. Chem. Soc., Dalton Trans.*, **1978**, 1314

[68] F. Huq, W. Mowat, A. C. Skapski, G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, **1971**, 1477

[69] P. Stavropoulos, P. D. Savage, R. P. Tooze, G. Wilkinson, B. Hussain, M. Montevalli, M. Hursthouse, *J. Chem. Soc., Dalton Trans.*, **1987**, 557 and references therein

[70] J. A. Halfen, S. Mahapatra, M. M. Olmstaed, William B. Tolman, *J. Am. Chem. Soc.*, **1994**, *116*, 2173

[71] A. Halfen, William B. Tolman, *J. Am. Chem. Soc.*, **1994**, *116*, 5475

[72] Samiran Mahapatra, Jason A. Halfen, Elizabeth C. Wilkinson, Gaofeng Pan, Christopher J. Cramer, Lawrence Que, Jr., William Tolman, *J. Am. Chem. Soc.*, **1995**, *117*, 8865

# Curriculum Vitae

Guido Seifert

## Biographical Data

| | |
|---|---|
| Birth date: | July, 10th 1964 |
| Place of Birth: | Berlin, Germany |
| Citizenship: | German |

## Education

### Doctoral Candidate

Technische Universität Berlin

July 1993 to Present

Priv.Doz.: Randolf D. Köhn, Ph.D.

### Dipl. Chem.

Freie Universität Berlin

Diploma in chemistry ("Hauptdiplom"), 1993

Thesis Title: Diffusion of Titanium in mono-crystalline Copper
(Diffusion von Titan in einkristallinem Kupfer)

Professor: G. Neumann, Ph.D.

"Vordiplom", 1988

### School

School in Berlin (Germany), 1971 - 1983

"Abitur", 1983

**Work Experience**

Freie Universität Berlin

Research assistant, 1990 - 1992

Technische Universität Berlin

Research assistant for Dr. Randolf Köhn, 1993-1998

**Languages**

English, Japanese

# List of Publications

1. Syntheses and Structures of 13-Substituted 1,5,9,-Triazatricyclo[7.3.1.$0^{5,13}$]-tridecanes and their Copper(II) Chloride Complexes

   Randolf D. Köhn*, Guido Seifert, and Gabriele Kociok-Köhn, Chem. Ber. **129** (1996), 21-24

2. Cationic zinc(II)alkyl complexes of N-alkylated-1,3,5-triazacyclohexanes and 13-benzyl-1,5,9-triazatricyclo[7.3.1.$0^{5,13}$]-tridecane

   Matthias Haufe, Randolf D. Köhn*, Roman Weimann, Guido Seifert, Dieter Zeigan, J. Organomet. Chem., **520** (1996) 121-129

3. Strained 1,3,5-Triazacyclohexane Complexes of Copper(I) and (II)

   R. D. Köhn*, G. Seifert, G. Kociok-Köhn, Chem. Ber., **129** (1996) 1327-1333

4. Solvent Dependent C-N Bond Length in a protonated Orthoamide,

   R. D. Köhn*, G. Seifert, G. Kociok-Köhn, Angew. Chem., **108** (1996) 3044-3046; Angew. Chem., Int. Ed. Engl., **35** (1996) 2879-2881